REMEDIATION OF FEEDLOT NUTRIENTS RUNOFF BY HYDROPONIC TREATMENT AND ELECTROLYSIS PROCESS

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Title

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

Intensive livestock farming in feedlot producing large amounts of manure and wastewater. Hydroponic and electrolysis treatments were studied for the remediation of nutrients from feedlot runoff.

Water hyacinth, water lettuce, and sorghum were hydroponically grown in 10 L of feedlot runoff and Hoagland solution individually in plastic bucket in batches in a greenhouse. All three plants performed well in uptaking NH_3-N (more than 90%) in feedlot runoff. From the feedlot runoff, TP reduction by sorghum, water hyacinth, and water lettuce ranged from 70% to 100% , 61% to 74%, and 49% to 93%, respectively.

With electrolysis process, 500 mL of feedlot runoff was treated with two rectangular parallel aluminum (Al-Al), iron (Fe-Fe), or hybrid (Al-Fe) electrode at 5 V, 10 V, and 15 V DC up to 30 minutes. The TP reductions were higher (100%) followed by COD (50 % to 75%) and TN (25% to 60%) by tested electrode.

Keywords: Hydroponic, feedlot runoff, nutrients, Hoagland solution, electrolysis, direct current, and specifc electrical energy consumption

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LIST OF ABBREVIATIONS

BMP…………………………Best Management Practice

BOD…………………………Biological Oxygen Demand

C……………………………Carbon

CAFO………………………Confined Animal Feeding Operation

COD…………………………Chemical Oxygen Demand

CRD…………………………Complete Random Design

DM………………………….Dry matter

E.Coli………………………. Escherichia coli

EC………………………….. Electrical Conductivity

FAO…………………………Food and Agriculture Organization

FS……………………………Fixed solids

ICP………………………….Inductively Coupled Plasma Spectroscopy

K……………………………Potassium

N……………………………Nitrogen

NaCl…………………………Sodium Chloride

NASS-USDA………………. National Agricultural Statistics Services, United States Department of Agriculture

NDAWN…………………… North Dakota Agricultural Weather Network

OP……………………………Orthophosphate

P……………………………. Phosphorus

PPM…………………………Part Per Million

P-value………………………Probability value

RO…………………………...Reverse Osmosis

TDS………………………….Total dissolve solid

TKN…………………………Total Kjeldahl Nitrogen

TN………………………… Total Nitrogen

TP……………………………Total Phosphorus

TS………………………….. Total Solid

UNDES…………………….. United Nations Department of Economic and Social Affairs

USEPA…………………… United State Environmental Protection Agency

V……………………………Voltage

VS……………………………Volatile Solid

$ZnCl_2$…………………………Zinc chloride

CHAPTER 1. GENERAL INTRODUCTION

1.1. Background

Livestock productions are increasing globally due to increasing demand of meat-based protein for increasing global populations. The same trend is also true in the United States. According to Mathews (2014), total red meat and poultry productions in the U.S from 2010 to 2013 were 92,097, 92,745, 92,963 and 93,326 million pounds, respectively, and the red meat production increased by 1.33 % from 2010 to 2013.

In the United States, as of January 2014, there are 87.7 million head of cattle, including calves. In North Dakota, as of January 2014, there are 1.8 million head of cattle and calves raised (NASS-USDA, 2014b). Confined animal feeding operations (CAFO) and their holding capacity have been increasing over the years. These CAFOs will generate large amounts of manure (*i.e.*, fecal and urinal waste along with feed, bedding, litter and soil) in a concentrated area. Manure and wastewater generated from the animal feeding operation are rich in macronutrients such as nitrogen, phosphorus and potassium, and organic matter. Similarly, manure also contains sediments, pathogens (such as *E. coli*), hormones, and antibiotics. Runoff and direct discharge of manure and wastewater may contaminate surface and groundwater if manure and wastewater are not manage properly. In particular, surface runoff of nitrogen and phosphorus in a fresh water body may help to accelerate eutrophication and reduce the oxygen level in water (Ansari et al., 2011; Hribar & Schultz, 2010). Therefore, from an ecological and environmental perspective, management practice(s) need to be adapted to reduce nutrients in runoff. Keeping that in mind, in this study, two management practices, namely hydroponics treatment and electrolysis process of runoff had studied.

1.2. Rationale of study

Feedlot runoff contains high nutrients content. If it is not manage properly, nutrient runoff may cause eutrophication (EPA, 2001; Hribar & Schultz, 2010; Koelmans et al., 2001). To reduce the negative environmental impact of feedlot runoff, United State Environment Protection Agency (USEPA) gives mandatory guidelines for discharging feedlot wastewater in the natural stream (Connor, 2010; Tiemann, 2011). Researchers are developing and testing different treatment options and technologies for wastewater treatment including membrane filtration, advance oxidation process, air floatation, distillation, evapotranspiration, nitrification, precipitation, ammonia stripping, electro dialysis (Bensadok et al., 2011; Ilhan et al., 2008). These methods are complex, sophisticated, expensive, and require specialized technical knowledge for remediation of feedlot wastewater (Crites et al., 2014). Moreover, themethods may not be economically viable for livestock growers (Kim et al., 2013). To combat the cost, scientists and researchers are continuously searching for alternative methods.

Among different biological treatments of wastewater, the hydroponictechnique is one of the treatment options that is usedor treating industrial and municipal wastewater. Researchers found that hydroponictechniques uptake greater amounts of soluble nutrients thus have a better reduction capacity than the vegetative buffer strips or other aerobic lagoon wastewater techniques (Jamuna & Noorjahan, 2009). Hydroponic tehcnique also requires minimum energy and cost and is environment friendly. Additionally, plants for their growth take up nutrients present in the feedlot runoff and development purposes. These nutrients can recovered after harvesting the plants' biomass, which can used as animal feed or other purposes such as in making paper, fiberboard, ropes, baskets, charcoal briquetting, fertilizer, and fish feed (Gopal, 1987). However, the use of hydroponics to treat feedlot runoff is limited. Therefore, this study has mainly focused on the treatment of feedlot runoff by utilizing aquatic (water hyacinth and water lettuce) and non-aquatic (sorghum) plants to remove nutrients from runoff.

Although hydroponics treatment of feedlot runoff are energy efficient, cost effective and environmental friendly, it takes longer than other feedlot runoff treatment processes (Bensadok et al., 2011). The electrolysis process works on the principle of oxidative or reductive chemistry and it needs relatively simple equipment at ambient temperature and pressure. Electrolysis is environmentally compatible, energy efficient, and this process required short treatment time and produced low amount of sludge (Chaturvedi, 2013; Inan & Alaydin, 2014). During electrolysis sludge is produced which can be used as fertilizer or used for extracting different valuable elements (Bridle & Skrypski-Mantele, 2000; Gaber et al., 2011; Sano et al., 2012; Sethu et al., 2008) and the effluent can be used for irrigation. In the past, limited research on the use of electrocoagulation were performed on livestock wastewater including swine (Bejan et al., 2007; Cho et al., 2010; Laridi et al., 2005; Rahman & Borhan, 2014), dairy (Bensadok et al., 2011; Şengil, 2006; Tchamango et al., 2010; Yavuz et al., 2011) and slaughter house wastewater (Bazrafshan et al., 2012) along with industrial effluents (Ali & Yaakob, 2012; Basha et al., 2008), pharmaceutical wastewater (Yi-zhong et al., 2002), agroindustry (Kim et al., 2013), and textile dye wastewater (Merzouk et al., 2009)**.** However, until today, electrolysis was not use to treat feedlot runoff. Therefore, this article investigated the electrolysis treatment of feedlot runoff in a batch under laboratory conditions using different electrodes at different applied electrical potential level.

1.3. Objectives

The objectives of this study were to reduce nutrients in feedlot runoff using two techniques, hydroponic treatment and electrolysis process. The specific objectives of these experiments are:

1 To determine net plant growth of water hyacinth, water lettuce and sorghum in different concentrations of feedlot runoff and Hoagland solution.

2 To determine and compare the nutrient uptake capacities and removal efficiencies of water hyacinth, water lettuce and sorghum plants from feedlot runoff and Hoagland solution.

3 To determine and compare the nutrients (TP, TN, and COD) concentration decreased by iron (Fe-Fe), aluminum (Al-Al), and hybrid (Fe-Al) electrodes from feedlot runoff at varying electrode potential level and treatment times.

4 To determine specific energy consumption per unit mass of nutrients (TP, TN, and COD) reduced or per unit volume of feedlot by three electrodes.

1.4. Hypotheses

The following hypotheses were tested during the experiments. The first two hypothesis were related to the remediation of feedlot nutrient runoff by hydroponics treatment and the last two hypothesis were related to the remediation of feedlot runoff by electrolysis.

- The water hyacinth, water lettuce and sorghum plants will be equally effective in removing nutrients from the Hoagland solution and feedlot runoff (undiluted, 1:1 and 1:2 dilution of runoff with reverse osmosis water).

- The water hyacinth, water lettuce and sorghum plants will make no difference in nutrient reduction over the treatment period.
- Al-Fe, Fe-Fe and Al-Al electrode have the same reduction capacity of TN, TP and COD from the feedlot runoff over electrolysis time.
- There will be no difference in specific energy consumption per unit mass of nutrients reduced by three electrodes during electrolysis.

CHAPTER 2. REVIEW OF LITERATURE

2.1. Livestock status and environmental concerns

Rapid increases in human global population and higher consumption of meat and dairy products have led to increased demand of livestock and poultry production. In 1999, the world population was 6 billion and it is projected that world population will reach 9.1 billion by 2050 (UNDESA, 2014). According to Thornton (2010), of the total calorie requirement for a human, livestock products occupied 17% of which 33% are meat based protein. Thornton (2010) reported that the total meat production in developing and developed nations increased from 45 million tons to 134 million tons and 88 million tons to 105 million tons, respectively since 1980 to 2002. Similarly, FAO (2013) reported that the world's meat production is expected to grow by 1.4% in 2013. According to Mathews (2014), total red meat and poultry production increased in the USA by 1.33% (from 41,775 to 42,332 million kilograms) between 2010 and 2013. As the populations of Africa and developing countries are increasing, the demand for meat-based protein is increasing due to higher income and urbanization (Thewis & Gali, 2012)**.** This increasing demand for meat-based protein will increase livestock production globally, thus increasing manure and wastewater.

In the United States, as of January 2014, there are 87.7 million head of cattle, among them 38.3 million have calved, 29 million are beef and 9.2 million are milking cows (NASS-USDA, 2014a). In the USA, beef cattle production is considered as an important livestock industry. In most cases, beef cattle are raised in feedlot or concentrated animal feeding operations and generate large amounts of manure (fecal and urinal waste along with feed, bedding, liter and soil) in a smaller area. The EPA (2001) and Cornwell et al. (2005) reported that feedlot runoff is one of the major sources of pollutant to lakes, rivers and fresh water reservoir. Therefore, manure and runoff generated from the animal feeding operation have high concentration of macronutrients such as nitrogen, phosphorus and potassium. They also contained organic matter, sediments, pathogen (such as E. coli), hormones, and antibiotics (Crane et al., 1983; Dillaha et al., 1989). If manure not manage properly, runoff from feedlot may contaminate in the surface water or groundwater, which may cause harmful effect to the environment.

2.2. Manure characteristics and nutrient contents

Animal manure consists of animal excreta along with dissolved water, mixed bedding materials or organic matter, which may use as an organic fertilizer. Depending on livestock species and housing systems, livestock manure usually collected as solids, semisolids, slurry, and liquid.

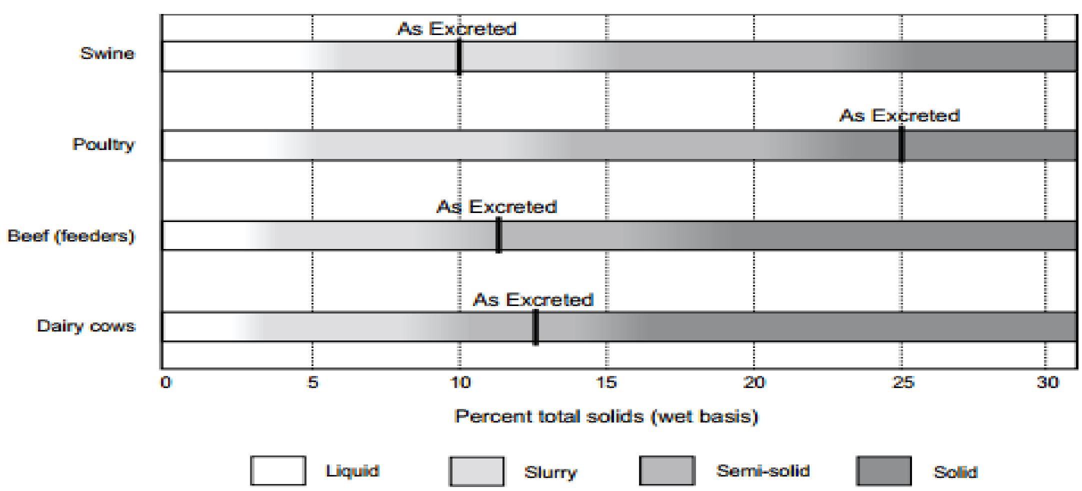

Figure 2.1. Consistency of various types of manure.
(Source: NRCS Agricultural waste management field handbook; (Nielson et al., 1996))

Manure properties depend on several factors such as animal species, diet, age and animal housing, and environment of the manure storage area (Kissinger et al., 2007; Yang, P. L. & Lorimor, 2000). Among animal species or types, their diet has a dominant effect on manure properties. Table 2.1 provides typical manure characteristics produced by 453 kg of beef cattle in one day, which had 88.4% moisture content.

Table 2.1. Typical manure composition produced by a total 453 kg of beef cattle with high forage diet conditions.

Description	Weight (kg/day/453 kg)
Manure	26.8
Total solids (TS)	3.071
Volatile solids (VS)	2.736
Fixed solids (FS)	0.335
Chemical oxygen demand (COD)	2.768
Biological oxygen demand (BOD)	0.616
Nitrogen (N)	0.593
Phosphorus (P)	0.050
Potassium (K)	4.983
C:N ratio	11

(Source: Spellman & Whiting, 2010)

Similarly, the characteristic of manure is also changed by animal housing type (Adriano, 1975). For beef cattle, there are many housing options depending on climatic conditions, but feedlots (confined outdoor housing) are common livestock production systems without constructing for collecting liquid or rainwater. However, depending on the state and federal regulations, livestock producers may construct runoff water collection system or treatment systems to minimize environmental concern such as surface water contamination (Gene Tinker, 2011).

The characteristics of manure also influence by bedding or litter, washed or spilled feed and water, soil etc. These factors basically change the physical or chemical characteristics of manure (Spellman & Whiting, 2010). Though the nutrient content in manure can change by different parameters, it has high value nutrients and can cause water pollution if it mix with fresh water. According to Spellman et al. (2010), in 1995, 37% of nitrogen and 65% of phosphorus contamination to the watershed were from the manure source in central United States.

2.3. Feedlot runoff characteristics and nutrient contents

Like manure, feedlot runoff has high nutrient concentration. According to Dickey & Vanderholm (1981), the average concentration of NH_3, TKN, P and K in feedlot settling basin effluent in Nebraska were 134, 300, 64.1 and 665 mgL^{-1}. Similarly, Rahman et al. (2013) analyzed feedlot wastewater collected from three counties in North Dakota over a two years period and reported that OP varies from 1.5 to 23 mgL^{-1}, TP from 4 to 80 mgL^{-1}, NH_4-N from 3 to 20 mgL^{-1}, NO_2-N+NO_3-N from 1.5 to 30 mgL^{-1}, TKN from 6.48 to 251 mgL^{-1} and K from 15 to 5074 mgL^{-1}. The concentration of nutrients in the feedlot runoff depends on the confinement density of the animals, animal's diets, surface slope (Albin, 1971), rainfall intensity, physical and topographic characteristics of a feedlot (Williams et al., 2006). However, it is also important to know the nutrient dynamics to reduce manure related environmental impacts.

2.4. Nutrients dynamics

Animal manure and runoff generated from feedlots contain nutrients. The nutrients contained in manure or in runoff are dynamic in nature and they undergo different physical, chemical and microbial process according to environmental factor such as heat, air, moisture and microbial activities (Habteselassie et al., 2006; Shi et al., 1999).

Nitrogen is considered as one of the most important macronutrient for the plants and it undergoes nitrification, denitrification, volatilization, ammonification and nitrogen fixation processes (Conley et al., 2009). In manure, nitrogen binds with protein and other complex compounds form that are not readily available to plants. By different metabolic activities, bacteria and fungi convert these organic forms of nitrogen through the ammonification process into ammonium nitrogen which is easily available for plants and other microorganism (Spellman & Whiting, 2010). The nitrogen present in the manure undergoes ammonia volatilization process which is affected by environment condition such as wind speed, moisture content of matter and temperature (Huijsmans et al., 2003).

Similarly, nitrification is an autotrophic microbial process in which nitrogen compound primarily NH_4-N sequentially oxidize to NO_2-N to NO_3-N form. In animal manure, significant nitrifying activity can develop during storage of manure, especially in deep litter and feedlot conditions (Sommer et al., 2003). In the first steps of nitrification process, the ammonia oxidize by nitrifying bacteria into nitrite form as shown in equation 2.1. In the second steps of nitrification process, the nitrate form of nitrogen oxidize by nitrifying bacteria into nitrate form as shown in equation 2.2.

$$NH_3+O_2 \rightarrow NO_2^-+3H^++2e^- \qquad (2.1)$$

$$NO_2^-+H_2O \rightarrow NO_3^-+2H^++2e^- \qquad (2.2)$$

Similarly, the denitrification process also facilitate by heterotrophic facultative anaerobic bacteria such as *Paracoccus denitrificans*. In the denitrification process, the nitrate nitrogen undergoes a series of reactions through the nitrite nitrogen, nitric oxide, nitrous oxide and finally into the nitrogen gas.

$$2NO_3^- +12H^++10e^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2+ 6H_2O \qquad (2.3)$$

Nitrogen fixation occurs by symbiotic or non-symbiotic bacteria and it fix atmospheric nitrogen into the ammonium nitrogen. Lightning also helps to fix the atmospheric nitrogen into ammonium nitrogen.

Three main pathways that cause nitrogen losses are denitrification, leaching and surface volatilization. Denitrification occurs due to heterotrophic facultative anaerobic bacteria. Therefore, the anaerobic condition created in soil is because of wet conditions, compaction, or warmer temperatures and cause denitrification process. Leaching is another cause of nitrogen loss that occurs with runoff. The NO_3-N is highly soluble and carried out with water. However, NH_4-N movement is slower because of positive ions of ammonium binds with negative ions of clay particles. Nitrogen loss also occur by volatilization, where nitrogen in manure changes into ammonia gas and pick up by the water vapor molecule. Nitrogen volatilization may affect by moisture level, temperature, and wind speed of environment and surface pH of the soil. Nitrogen may lost by surface runoff from feedlot or following the application of manure to cropland.

Phosphorus is the second most required nutrients for plants after nitrogen because it is an essential element for energy and genetic transfer through photosynthesis and nucleic acid formation. Phosphorus occurs in soil and minerals, living organisms, and water from +1 oxidation state to +5 oxidation state. Phosphorus availability is low due to slow diffusion and high fixation in soils. It undergoes mineralization, immobilization, sorption, desorption, precipitation, dissolution and leaching process in soil process (Shen et al., 2011). Generally, phosphates are in three forms: orthophosphate, active phosphate and fixed phosphate. The orthophosphate is the simplest phosphate which is found in soluble organic form and readily available for the plants but it is not easily formed and insufficient to supply for plants' demand because it is quickly taken up by plants and takes time to replete it again. In soil, active phosphate is the second form of phosphorus and generally found in an inorganic solid form and it can easily release plant available phosphorus to the soil and contributes most of phosphate demand of plants. The active phosphate particles mostly attach to small soil particles, reacts with calcium or aluminum, and forms soluble solids. Soil particles act as a source or sink for the phosphate depending on surrounding water condition. Soil can provide phosphate when surrounding water has low level of adsorbed phosphorus and vice versa (Busman, 2009). The third type of soil available phosphate is fixed phosphate, which usually does not help fertility of soil due to its very slow availability and almost inert nature. The inorganic phosphate, which usually occur in insoluble crystalline form. The organic phosphate, which occurs in plant or animal tissue, does not undergo mineralization easily by microorganisms.

Usually, phosphorus strongly bind with soil particles, resulting in low P leaching losses from soils. However, significant P losses may occur along with soil particles by runoff from feedlot or soil surface. Phosphorus losses from feedlot or from land may reduce through best management practices or treatment technologies.

Plants absorb potassium in ionic form (K^+) from the soil. The main role of potassium is to regulate metabolic processes, protein synthesis, photosynthesis, and turgidity. According to Biswas (2008), potassium has higher polarizability due to the weak bond between potassium and oxygen and prefers ion exchange reaction with water. Potassium generally have in four forms: soluble, exchangeable, fixed and mineral potassium and changes from one form to another form when dissolve in water.

2.5. Nutrients transport and water pollution

Livestock manure mainly contains nutrients (nitrogen, phosphorus, and potassium), organic matter, solids, pathogens (*E. coli, Salmonella*) and volatile odorous compounds (Crane et al., 1983; Dillaha et al., 1989). Nutrients present in manure may transport into fresh water through runoff from two sources: I) from land application of manure, and II) feedlot manure exposed to rainfall directly. Nutrient and organic matter losses to surface waters through runoff may cause eutrophication and algal bloom. In the following sections, nutrient transport mechanisms, especially N and P, have described.

2.5.1. Phosphorus transport

Phosphorus primarily occur on earth as phosphate form in inorganic phosphate rock, which is nonrenewable and depleting continuously. Phosphate also occurs in organic form in animal and plant tissues. Water is the main carrier of phosphate. Surface and subsurface flow transports the soluble phosphate presents in agricultural fields, manure piles and feedlot areas, phosphate mining or phosphate rocks. Flood or erosion carry the insoluble phosphate bind with particles along with sediment. Similarly, organic phosphate bind with plants, animals, and animal wastes carry into the water body by the water transportation, which shown in Figure 2.2. Excess soil particle-bound P or soluble phosphate runoff into surface water can cause nutrient losses and eutrophication, which may be reduced through best management practices (BMPs) or treatment technologies.

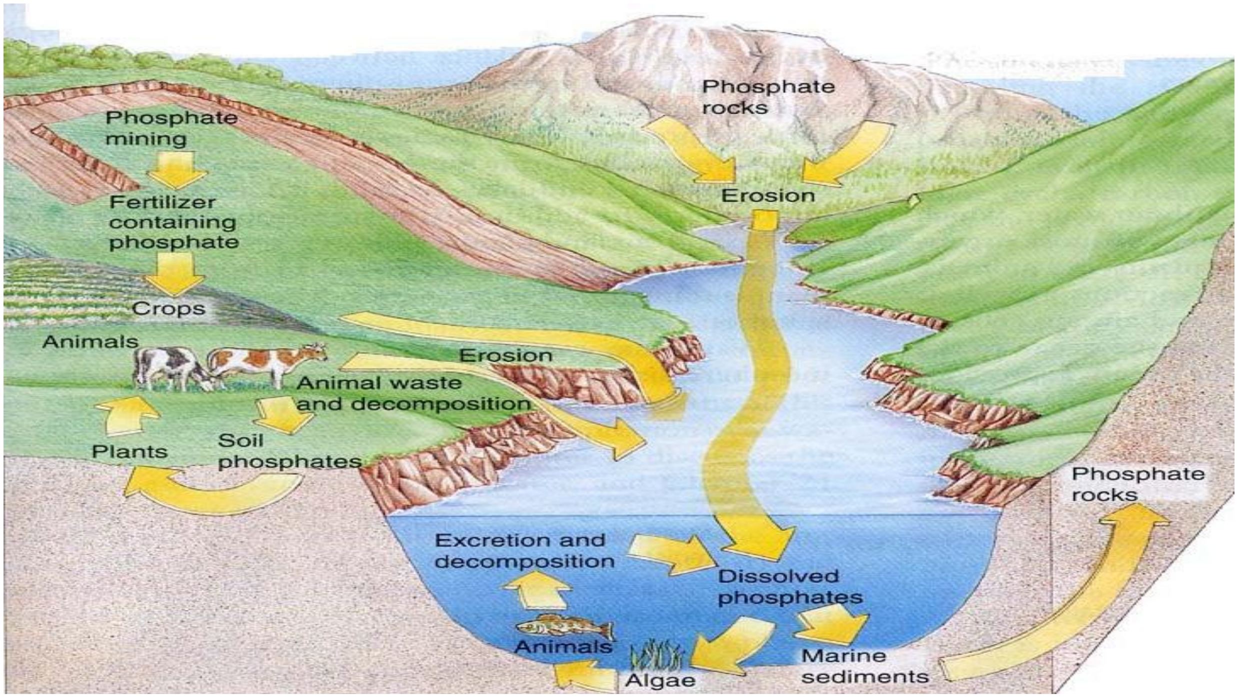

Figure 2.2. Phosphorus cycle.
Photo credit: Raven, Peter, Linda Berg (Raven, 2001)

2.5.2. Nitrogen transport

Nitrogen is very dynamic in nature and can be transported physically, chemically and biochemically (Figure 2.3). Nitrogen easily undergoes redox reaction through chemical and biochemical reactions. The oxidation state of nitrogen varies from a +5 state in the nitrate anion to -3 state in the ammonium cation (Pierzynski et al., 2005). Atmospheric inert nitrogen is the main source of nitrogen, but in practical conditions, this source is not readily available to plants. Only a small amount of atmospheric nitrogen undergoes lightning and bacterial fixation. Therefore, inorganic fertilizer or organic manure fertilizer is applied into the field to boost crop yield. Applied fertilizer, manure, and plants and animal biomass, contain different forms of nitrogen, which undergo nitrification and denitrification process. Plants take up portions of nitrogen and some are lost during the nitrification and denitrification process, and some are lost to runoff or leaching, causing environmental concerns on water pollution.

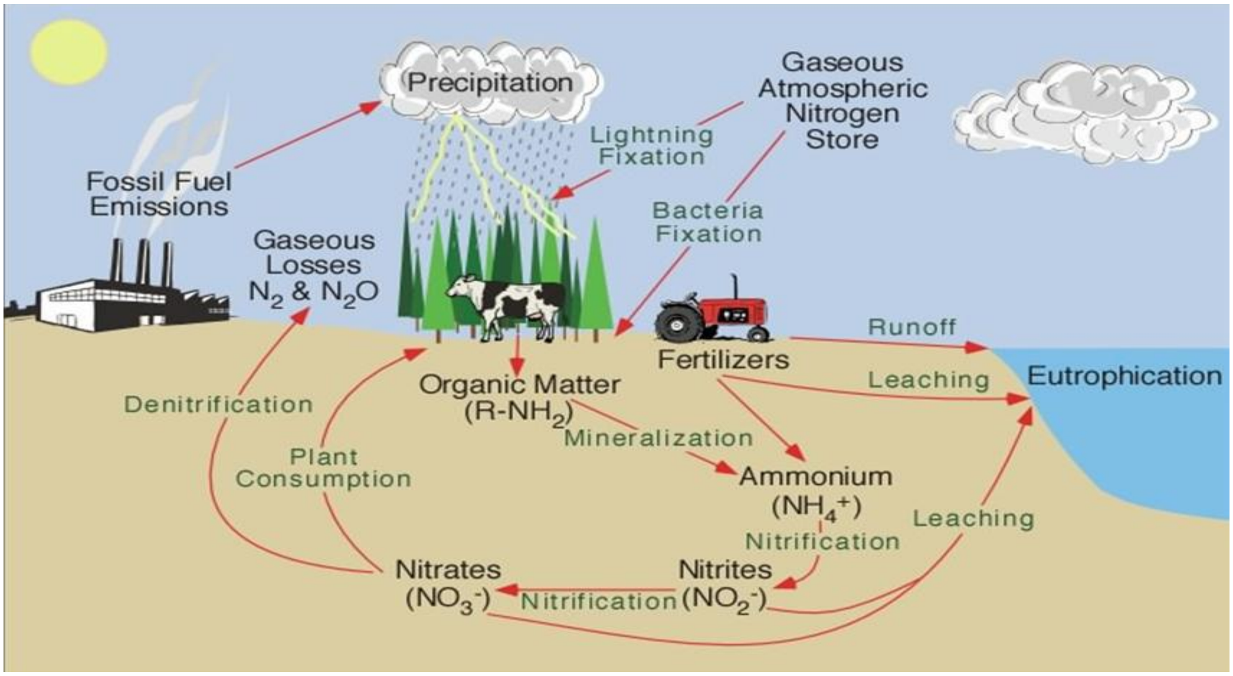

Figure 2.3. Nitrogen cycle.
(Photo credit: Pidwirny, 2006)

2.6. Water pollution mechanisms due to transported nutrients

Animal feeding operations are significant sources of water pollution. From the twenty-two state's survey data, it was reported that 20% of the river's and streams' pollution was contributed by intensive animal feeding operation among different agricultural operations. Excess concentration of nitrogen and phosphorus in surface water causes vigorous growth of plants and aquatic animals and causes eutrophication and hypoxia of lagoons and estuaries, and affect the sanitary nature of the environment (Dale & Polasky, 2007). Additionally, excessive nutrients also promote bacteria and algal bloom. Cyanobacteria, also known as blue green algae, may produce cyanotoxins which is harmful to human and animals (Manganelli et al., 2012).

The phosphorus generated from the feedlot runoff can exist in various phosphate species, which are classified as orthophosphates or soluble phosphate, active phosphates, and fixed phosphates (Busman, 2009). Orthophosphate is mainly available in dissolved form and can meet the phosphate demand of plants and microorganism readily. Therefore, orthophosphate is the main concern for all scientist and researchers but other types of phosphorus cannot be ignored totally because they also provide phosphate slowly (Jenkins et al., 1971).

Nitrogen is also present in soil and water in different forms such as nitrate, nitrite, and ammonium nitrogen as described before. Sometimes, these forms of nitrogen change due to nitrification and denitrification processes and supply nutrients to plants and microorganisms. The phosphate and nitrogen in the feedlot wastewater or runoff may cause eutrophication and hypoxia in lagoon and estuaries that can kill fish and can cause methaemoglobinemia known as blue baby syndrome. Blue baby syndrome usually occurs when infants consumed more than 10 mg/L nitrate nitrogen containing water (Knobeloch et al., 2000).

Eutrophication is also synonymous with autotrophic algae blooming in water. According to Yang et al. (2008) the analysis of algae bioplasm provides the following equation.

$$106CO_2 + 16NO_3^- + HPO_2^{2-} + 122H_2O + 18H^+ \xrightarrow{\text{Energy+micronutrient}} C_{106}H_{263}O_{110}N_{16}P \text{ (bioplasm of algae} + 138O_2) \quad (2.4)$$

This equation reveals that inorganic nitrogen and phosphorus are playing a vital role for algae growth. The molecular ratio of carbon, nitrogen and phosphorus in phytoplankton algae is 106:16:1 (Redfield, 1934). This ratio shown that if phosphorus can limit in the water, the growth of algae can controlled because nitrogen and carbon from the atmosphere can contaminate waster easily. Sharpley (2001) also mentions that controlling phosphorus contamination to freshwater can reduce eutrophication.

2.7. Management and treatment process of feedlot runoff

Runoff generated from feedlots contains high nutrients, organic matter, and pathogens. Some of these pollutants can be managed and treated by a single step process up to multi step processes depending on the condition of wastewater, remediation technology and requirement of final water quality (Group, 2014). In most cases, the treatment of wastewater contains more than one process to obtain desired water quality. Wastewater treatment processes can be classified into physical, chemical and biological process (EPA, 2004).

In physical treatment processes, wastewater is treated by sedimentation, screening, aeration, filtration, membrane filtration, floatation, or degasification. In the sedimentation process, the heaver sediment particles settled down due to gravity in quiescent condition. Similarly, screening and filtration process help to remove the debris and large solid particles when wastewater passed through screen. With filtering and sedimentation, sediment bound nutrient, especially phosphorus, can be reduced from runoff or wastewater.

In chemical treatment process, chemicals are used so that waste material can be separated or precipitated easily from the water. The most popular chemical treatment methods are chlorination, ozonization, chemical coagulation, electrolysis, adsorption, ions exchange and neutralization (EPA, 2004). In chlorination and ozonization methods, chlorine and ozone are applied to the wastewater so that the chlorine and ozone kills the bacteria and proceed a redox reaction due to its oxidation property that helps to reduce pollutants from the water. In chemical coagulation, alum, lime or ferric chloride are used which help to coagulate the solid particles present in the water. During chemical coagulation, solid particles change to an insoluble product due to the chemical bonding with coagulant or neutralizing the charge present in the solid particle by the coagulant. In the ion exchange method, the divalent or trivalent metal and sometimes an electrolysis process are used to help precipitate nutrient ions from the wastewater.

In biological treatment processes, mostly microorganisms, plants and algae are used to treat the wastewater under aerobic and anaerobic condition. The aerobic and anaerobic microorganisms consume organic matter present in the wastewater as food and convert waste into different stable by-products, which can easily separate from the wastewater. Similarly, when plants and algae are planted into wastewater, they uptake soluble nutrients from the wastewater and helps to purify wastewater (EPA, 2004).

There are also large numbers of classical and advanced wastewater treatment techniques such as air floatation, distillation, facultative lagoon, membrane process, evapotranspiration, nitrification, precipitation, ammonia stripping, electro dialysis, or advance oxidation (Bensadok et al., 2011; Ilhan et al., 2008). However, these techniques are not economical for diffuse or nonpoint source pollution due to scale of operation and investment costs (Crites et al., 2014).

Treating feedlot runoff, vegetative filter strips or buffer strips are commonly used as low cost technology, but maintenance is needed. The principle of vegetative filter strips/buffer strips are to dissipate wastewater after passing through the vegetation, reduce surface runoff and increase infiltration of runoff and nutrients, promote sediment deposition, filtration and provide nutrient uptake by the plants (Dickey & Vanderholm, 1981) . According to Dillaha et al. (1989) and Rahman et al. (2013), the vegetative filter strips are only effective for the sediment and sediment bounded nutrients but not soluble nutrients. To eliminate the drawback of vegetative filter strips, alternative methods of feedlot runoff treatment techniques (hydroponics and electrolysis) have been studied in this research and discussed in the following sections.

2.8. Remediation of feedlot runoff by plants as best management practices

According to the EPA the best management practice are activities, maintenance procedures and management practices used to prevent or reduce the pollution of wastewater (Service, 2014). Wastewater treatment techniques such as constructing solid separators and treatment ponds, vegetative filter strips, and membrane filtration have been introduced. Though they are successively used for treatment of wastewater, they have limitations. Solid separators and treatment ponds can separate solid particles, but cannot separate soluble nutrients. Similarly, membrane filtration techniques require electricity to run the pump and requires a high initial investment, running and operating costs. After realizing these limitations, hydroponics techniques for wastewater treatment was tried for implementation in this research. Hydroponics technique is one BMP practiced to reduce soluble nutrients, require less or minimum energy, has minimal chemical risks, and restores biodiversity of plants (Wolverton & McKown, 1976). The same technique can be used to treat feedlot runoff.

To reduce the soluble nutrients from wastewater, researchers are using different plant varieties based on the adaption capacity of plants in wastewater and its biomass production and nutrient reduction capacity (Gupta et al., 2012). Based on available literature, water hyacinth (Brix & Schierup, 1989; Gupta et al., 2012; Ndimele & Ndimele, 2013; Spencer et al., 2006), water lettuce (Gupta et al., 2012; Koné et al., 2002; Snow & Ghaly, 2008) and sorghum (Khan et al., 2010; Lobato et al., 2008; Oliveira Neto et al., 2009; Yang, Y. et al., 1990) plants have high salt tolerance. Therefore, these three types of plants were selected in this study.

2.8.1. Feedlot runoff salinity level and salt tolerance mechanism of plants

Salinity is the concentration of dissolve salts in water. High salinity means high mineral salt and most probably high sodium ions. High salinity can create physiological drought conditions and ion toxicity (Xiong & Zhu, 2001; Zhu, 2001). Therefore, high sodium is toxic to cell metabolism and suppress the activity of essential enzymes, cell division and osmotic imbalance and finally suppresses the growth of plants (Tuteja & Mahajan, 2007).

Generally, in feedlot wastewater runoff, salinity range values vary according to rainfall, animal density, topographic conditions and feedlot management. According to Rahman et al. (2013), the salinity level of feedlot runoff in North Dakota ranged 0.701±0.501 $mScm^{-1}$ to 4.740±2.873 $mScm^{-1}$. Sweeten (1990) reported that the salinity level of runoff generated from the feed yard in Texas from 6 to 8 $mScm^{-1}$.

According to Kotuby et al. (1997), soil salinity is categorized based on plant response. In a non-saline soil class, electrical conductivity ranges between 0-2 $mScm^{-1}$ and salinity effects on plants are considered mostly negligible. In a slightly saline soil class, the electrical conductivity is from 2-4 $mScm^{-1}$ and growth of sensitive plants is restricted. Similarly, in a moderately saline soil class, electrical conductivity ranges between 4-8 $mScm^{-1}$ and growth of plants are restricted. Likewise, in strongly saline soil, electrical conductivity ranges between 8-16 $mScm^{-1}$ and only salt tolerant plants can grow. Above 16 $mScm^{-1}$ soil salinity is classified as very strong saline soil and few very tolerant plants grow satisfactorily.

Though plants suffer severely from the salinity, many plants have a persistent capability to survive in salt water using different anatomical and morphological adaptation mechanisms. Most of the plants use salt exclusion, salt excretion, succulence, osmotic adjustment and membrane composition mechanism for the salt tolerance and can adjust to saline conditions

(Greenway & Munns, 1980; Munns & Tester, 2008). In a salt exclusion process, plants exclude salt from entering through the root system and restricted it from sensitive parts of the plant (Carillo et al., 2011). In salt excretion, plants excrete excess salts through their roots, shoots and leaves. Some plants transport and accumulate excessive salts to storage areas as well (Horie et al., 2012). In succulence, the salt concentration of plants can dilute by taking up more water. This phenomenon is only possible in wetlands where water is abundant. In osmotic adjustment, salt is accumulate in vacuoles and protects the proteins and cell membrane from the ion toxicity. During this process, osmotically active organic solutes help to maintain osmotic balance with cell cytoplasm (Jefferies, 1981). Compositions of plasma membrane such as membrane lipid, aquaporin and proton pumps in the roots cell can be changed for the adaptation of plants to saline conditions (Pérez-Pérez et al., 2009).

Therefore, salinity is the main limitation to treat feedlot runoff using plants. During plant selection for treatment of feedlot wastewater, salt tolerant plants should be selected and used in this study.

2.8.2. Nutrient uptake mechanism of plants

Plants nutrients are broadly categorized into macronutrients and micronutrients. Macronutrients are considered the main constituents of plants. They are needed for the formation of protein, nucleic acids, and carbohydrate during cell development and physical activities. Nitrogen, phosphorus, potassium, magnesium, calcium, sulfur, carbon, hydrogen and oxygen are the macronutrients. Micronutrients are needed for regulation of different enzymatic activities and include iron, zinc, manganese, copper, boron, molybdenum, nickel and chlorine (Morgan & Connolly, 2013). According to Matimati et al. (2013) and Oliveira et al. (2010), the above mention nutrients and water are taken up by the plants through root interception, mass flow and diffusion. The active and passive transport system of cells during nutrient uptake of nutrients also govern. Root interception: when nutrient contact with the root surface area, interception of nutrient occurs. Therefore, interception is directly proportional to the root surface area. Mainly calcium, magnesium, zinc and manganese are intercepted into the plant.

Mass flow: It occurs when the potential gradient generated by the evapo-transpiration of plants. The potential gradient helps to uptake water and dissolve nutrient by the plants. Mostly, nitrogen, calcium, magnesium, sulfur, copper, boron, manganese and molybdenum move to the root by mass flow.

Diffusion: It occurs due to the concentration gradient from high to lower concentration. It is a slower process than mass flow and diffusion and delivers appreciable amounts of phosphorus, potassium, zinc and iron to the root surface. Plants symbiosis with microorganisms also helps to nutrients uptake.

2.8.3. General characteristics and nutrient reduction capacity of plants

In hydroponics, plants absorb nutrients from water through their effective root system, which directly helps to improve the water quality. Municipal wastewater, industrial and anaerobically digested flush dairy manure wastewater (ADFDMW) has been treated hydroponically using different plants. According to Sooknah & Wilkie (2004) macrophytes such as water hyacinth, pennyworth, water lettuce and polyculture in 1:1 diluted anaerobically digested flush dairy manure wastewater can uptake nutrients significantly. Similarly, Reddy et al. (1984) reported that nitrogen removal by aquatic plants in descending order were water hyacinth> water lettuce> pennyworth > Lemna during summer season, while pennywort> water hyacinth> Lemna > water lettuce in winter. Phosphorus removal in the summer was highest by water hyacinth, while pennywort removed the highest amount in the winter. This nutrient reduction order is due to greater growth of water hyacinth and water lettuce in summer but pennyworth in winter. Similarly, sorghum can tolerate moderately saline water (Rani et al., 2012) and used for treatment of saline water. Following sections will discuss some of the characteristics of these plants.

2.8.3.1. Water hyacinth (*Eichhornia crassipes*) and nutrient reduction capacity

Water hyacinth is a surface floating perennial aquatic plant. Water hyacinth has ovate, thick, leaves and long, spongy petioles. Its size depends on growing conditions and is generally from 0.2 cm to 0.5 cm (Petrell et al., 1994). It floats on the surface of water as well as on the surface of moist soil. The roots of water hyacinth are brown fibrous, generally 0.04 m to 0.22 m in length in water. Water hyacinth can grow healthily at tropical and subtropical climates having a temperature range between 28 °C -30 °C (Gupta et al., 2012). Generally the plant grows optimally at pH 5.8 to 6 but can tolerate a highly acidic pH range of 4 to alkaline pH 8 (El-Gendy et al., 2004). According to Makhanu (1997), water hyacinth contains 95% water and 5% dry matter. The dry matter is 50% silica, 30% potassium, 15% nitrogen and 5% protein. The growth also strongly depends on the dissolved major nutrients, for example, nitrogen and phosphorus. The growth rate also depends upon the photosynthesis capacity of the plant, solar light intensity, leaf characteristics and stem height (Li et al., 2011). The water hyacinth's optimal growth rate was 28 mgL^{-1} total nitrogen level and 7.7 mgL^{-1} phosphorus level (Gupta et al., 2012). However, according to Reddy (1989, 1990; 1991), water hyacinth growth is optimum when N, P, and K concentrations are 5.5, 1.06, and 22 mgL^{-1}, respectively. When the concentration of nutrients increases, it store them in the tissues. Reddy (1989, 1990; 1991) also mention that water hyacinth withstand up to 50.5 mgL^{-1} nitrogen, 10.06 mgL^{-1} phosphorus and 52 mgL^{-1} potassium and it store in the tissues. Knipling et al. (1970) found that water hyacinth plants in low-phosphorus environments of 0.05 mgL^{-1} had larger root to shoot ratios than plants in high phosphorus water of 0.5 mgL^{-1}.

Warm climates such as tropical and subtropical areas are favorable for the growth of water hyacinth. The application of water hyacinth is more suitable for the point and non-point source pollutant, which lies, in tropical rather than subtropical climate. High nutrient containing wastewater, good temperature range and longer daylight influence the photosynthesis rate and increase the growth of plants. Reddy & DeBusk (1984) observed water hyacinth can grow from 47 to 106 tons of dry mass per hectare per year. Approximately 50% of biomass was produced during May through August. In poor nutrient waste approximately 50% was root but it was only about 25% in high nutrient water.

Sooknah & Wilkie (2004) studied growth of water hyacinth, water lettuce and pennywort in anaerobically digested dairy manure wastewater runoff without dilution and they found that except hyacinth all the plants died. However, when they diluted wastewater with water in 1:1 ratio, all the plants grew well and water hyacinth showed more robust growth than others did. These plants were also able to reduce nutrients such as total Kjeldahl nitrogen (TKN), TP, NH_4-N, and soluble reactive phosphorus by more than 90% in one month.

Reddy & DeBusk (1984) studied water hyacinth by constructing a pond with a retention time of 7 days and found that nitrogen reduction was more than 50%, phosphorus reduction was 40-50% and mass production was 690 kg to 1060 kg dry weight per day from a 2.65 ha and 1 m depth pond. Henry-Silva & Camargo (2006) grew water hyacinth and water lettuce and found that total phosphorus reduction was more than nitrogen at 80% and 40% increases, respectively.

According to Gopal (1987), water hyacinths also may be used for removing heavy metal and microorganism. Sooknah & Wilkie (2004) reported that 54% and 89% reduction of electrical conductivity (EC) from the diluted and undiluted flush dairy wastewater due to the absorption of Na^+ concentration. Additionally, Wolverton & McKown (1976) reported that water hyacinth can also remove phenol.

2.8.3.2. Water lettuce (*Postia stratiotes*) and nutrient reduction capacity

Water lettuce is a perennial monocotyledon plant with thick, soft leaves on the surface of water and forms a rosette shape. The leaves are up to 0.15 m and plants resemble ordinary lettuce but have no stem. The roots hanging submerged beneath floating leaves. It's optimum growing conditions area climate such as tropical and subtropical areas and free floating in still or slow moving water bodies such as dams, reservoirs, lakes and creeks. The small tiny flowers do not appear easily when the flower is inside the leaves. This plant can reproduce vegetative propagation. Seeds can survive at 4 °C water temperature and germinate readily in 25 °C water temperature if light penetrates into the water (Parsons & Cuthbertson, 2001). Water lettuce is not winter-hardy and grows optimally at 25 °C to 35 °C (Victor, 2001).

The specific growth rate of water lettuce was slight higher in dry season, and in rainy season than winter season. In the winter season, the growth rate of water hyacinth decreased almost 70%, but the rate of water lettuce decreased only 45%. From these results, water lettuce is thought to be grown up enough even under low solar radiation. The nitrogen, phosphorus and ash continents of biomass were about 1.65%, 1.03% and 19.9%, respectively, and biomass of water lettuce is not so big and heavy which can easily remove during surplus biomass from the water body (Aoi & Hayashi, 1996). Water lettuce growth severely decreased at salinity levels above 1.66 ppt, resulting in mortality at levels above 2.50 mgL^{-1} (Haller et al., 1974).

Fonkou et al. (2002) reported average nutrients contents in the water lettuce biomass as 4.72% (DM) TKN, 30.91% (DM) Crude protein, 5.6% (DM) crude fat, 15.14% (DM) crude fiber and 19.72% (DM) ash. Water lettuce doubles its biomass in just over 5 days; triples it in 10 days; quadruples in 20 days and has its original biomass multiplied by a factor of 9 in less than one month. This indicated that 25 days is the maximum growing period for water lettuce in the hydroponics system. In addition, one quarter of each pond should be harvested every 15 days because water lettuce reproduces rapidly and decays without proper management. Physicochemical parameters are reduced progressively from the influent to effluent ponds. Particularly, turbidity, phosphates, total iron, sulfates, color, COD, BOD, Suspended solids, dissolved oxygen and nitrates are improved by more than 70%.

Awuah et al. (2004) used water lettuce in a continuous flow of sewage. They reported fecal coliform removal was log 6 and sediment was reduced by 99%, biochemical oxygen demand (BOD) by 93%, chemical oxygen demand (COD) by 59%, nitrate by 70%, total phosphorus (TP) by 33%, ammonia by 95% and TDS by 70%. Sooknah & Wilkie (2004) studied water lettuce growth in 1:1 diluted anaerobically digested dairy manure for one month and found that ammonium nitrate was reduced by 99.2% and electrical conductivity and alkalinity were reduced by 35%.

2.8.3.3. Sorghum (*Sorghum bicolor*)

Sorghum belongs to the grass family and is cultivated for fodder and grain for animal and human consumption. Sorghum physically appears similar to corn before flowering. Sorghum produces more tiller and fibrous root systems than corn. Sorghum has roots, node, inter-node, leaves, a panicle with spikelet, and normally self-fertilizes. Sorghum seed color varies depending on the variety of plant In most cases seeds are white and brown in color (Carter et al., 1989). Grain sorghum become 0.9-1.5 m tall and low dry matter but forage sorghum become 1.8 m to 3.6 m tall and having high dry matter and mainly used for silage. The other cross breeds are between to these height and used for grain as well as silage production (Undersander et al., 1990).

Sorghum is staple food for the human consumption and animal feed. Most research on sorghum is in regard to production but very few related to effect of heavy metal on growth rate of sorghum (Masarovič et al., 2012). Irrigation of waste stabilized pond effluent and its effect on growth and yield has been studied (Khan et al., 2010). This research was based on sorghum grown in the soil but not under soilless hydroponics condition. Therefore, to determine the nutrient reduction capacity of sorghum typically from wastewater is difficult and it is necessary to analyze the soil nutrients before and after cultivating sorghum at optimum vegetative growth and crop yield. The optimum crop yield is determined by applying different rates of macro and micronutrients into the soil. According to Carter et al. (1989), 100 bushels of sorghum yield required 100 pounds of nitrogen, 14 pounds of phosphate and 14 pounds potash per acre (3.5 m^3 sorghum by 32.6 kg-N, 4.56 kg-P, 4.56 kg-K in 0.4047 ha).

According to Ferguson (2000), the amount of nitrogen required to produce 200 bushels of sorghum in soil containing 3% organic matter and 2 ppm nitrogen was 200 pounds of nitrogen, soil with 6-25 ppm phosphorus required 20-40 pounds phosphorus and soil containing 41-75 ppm potash required 60 pounds of potassium fertilizer per acre.

According to Franzen et al. (2011), to achieve 3 tons per acre of sorghum forage production, nitrogen requirements were 75 pounds per acre (34 kg per 0.4047 hectares), phosphorus was 30 pounds per acre (13.607 kg per 0.4047 hectares) and potassium was 115 pounds per acre (52.1631 kg per hectares). Similarly, for the production of 9 tons of forage, nitrogen requirement was 225 pounds (102.05 kg), phosphorus was 90 pounds (40.82 kg) and potassium was 333 pounds (151.04 kg) per acre (0.4047 hectares) in North Dakota. Fertilizer requirements for grain sorghum were slightly different from the forage sorghum. For the production of 60 bushel per acre (2.114 m^3 per 0.4047 hectare) nitrogen requirement was 66 pounds (29.93 kg), phosphorus requirements was 36 pounds (16.33 kg) and potassium requirements was 46 pounds (20.86 kg). To achieve production of 120 bushels per acre (4.23 m^3 per 0.4047 hectares), nitrogen requirement was 132 pounds (59.87 kg), phosphorus requirement was 72 pounds (32.65 kg) and potassium requirement was 91 pounds (41.27 kg) per acre (per 0.4047 hectare) in North Dakota.

The bulk of evidence seems to indicate that grain sorghum is only moderately tolerant of salinity, being less tolerant than wheat, cotton or barley (Eaton, 1942; Hart, 1974). Francois (1984) reported that grain sorghum cultivars Double TX and NK-265 were unaffected up to a soil salinity of 6.8 $mScm^{-1}$. Each unit increase in salinity above 6.8 $mScm^{-1}$ reduced yield by 16%. Similarly, an EC value (saturation extract) of 12 $mScm^{-1}$ was required for 50% yield reduction (Hart, 1974). Azhar & McNeilly (2014b) suggested the existence of differences among sorghum cultivars in tolerance to salinity.

Therefore, during crop selection for feedlot nutrient runoff remediation, the salt tolerance capacity of a crop should be consider. From the literature, sorghum falls in the moderate salt tolerance range and can grow in saline soils. During hydroponics cultivation of plants, plants should tolerate waterlogged conditions. From the study, sorghum seems to be more tolerant of wet soils and flooding than most of the grain crops (Carter et al., 1989).

2.8.4. Uses of water hyacinth, water lettuce and sorghum

From the literature water hyacinth and water lettuce are considered noxious and harmful, and some places it is band to transfer them due to their adaptive capacity and excessive growth rate in variable conditions. Many researcher have been involved in studies to eradicate and control water hyacinth and water lettuce. According to Wolverton & McDonald (1979), water hyacinth and water lettuce are the low cost technology as compared to advanced wastewater treatment and they consume little or no external energy. Beside these, water hyacinth and water lettuce have different uses as follows:

According to Nigam (2002), water hyacinth and water lettuces can be used for biofuels and it is very useful source of renewable energy. Conventional energy sources in the world are depleting due to high-energy demand and biofuel demand for the replacement of conventional energy is increasing daily. Therefore, these plants can be used for the remediation of feedlot nutrient runoff as well as used for the raw material for biofuels.

According to Tucker & Debusk (1981), water hyacinth and water lettuce biomass are used for methane production through anaerobic decomposition. In some places, production of methane is applicable in large scale because of its high yearly average net productivity. Reports indicated that water lettuce biomass has potential to produce methane because of its adequate nutritive value for the biomass to methane conversion (Tucker & Debusk, 1981). Additionally, Gopal (1987) reported that water hyacinth and water lettuce biomass may be used for making paper, fiberboard, rope, basket, charcoal briquetting, animal fodder, fertilizer, and fish feed.

Similarly, sorghum is useful for different purposes. Sorghum is the fifth most important crop in the world after wheat, rice, maize and barley. It is grown on 42 million hectares in 98 countries and is a basic food for 500 million people around the world. Africa produces about 59% of the total sorghum, followed by Asia (25%), North America (11%), South America (4%) and Europe (1%) (Tamas, 2009). In the United States, South America, and Australia, sorghum use for livestock feed and ethanol production. Whereas, in other countries, sorghum is used as human food.

2.8.5. Role of light intensity and duration for plant growth

Light is the important source of energy to trigger the photosynthesis of plants along with carbon dioxide, nutrient and water. The energy contained in light is absorbed in the chlorophyll of plants during photosynthesis. Therefore, the photosynthesis of plant influence by light intensity and duration. Light intensity is simply the total amount of light received per unit time. Light duration refers to the amount of time that a plant is exposed to sunlight. The higher the light duration and light intensity, the greater the chance of photosynthesis for the plants. Higher rates of photosynthesis means greater amounts of food production for the plant, which ultimately affects the plant growth and development. The higher the photosynthetic rate means more nutrients from the water or soil media take up through the root system. The higher uptake up nutrient from wastewater means the reduction of nutrient pollutants in wastewater, thus It helps to purify wastewater.

2.9. Remediation of feedlot wastewater by electrolysis

Though biological treatment processes such as conventional aerobic lagoons and hydroponics techniques are effective, these techniques are time consuming for the treatment of wastewater and cannot remediate large volumes of water in small areas efficiently (Bensadok et al., 2011). Scientists are trying alternative techniques of wastewater treatment process and electrolysis is one of option for feedlot runoff treatment process. This techniques has been used for remediation of industrial effluents (Ali & Yaakob, 2012; Basha et al., 2008), slaughter house wastewater (Bazrafshan et al., 2012), dairy wastewater (Tocchi et al., 2013), olive oil mill wastewater (Inan et al., 2004), pharmaceutical wastewater (Yi-zhong et al., 2002) agroindustry (Kim et al., 2013), textile dye wastewater (Merzouk et al., 2009) etc. It has several advantages, such as a simple design, requires less energy, water can be treated within a few minutes or hours, sludge can be used as fertilizer and can be recovered if it has valuable elements.

2.9.1. Introduction of the electrolysis process

In the electrolysis process, wastewater is treated by using direct currents through a pair of metal electrodes at ambient temperature and pressure. Metal ions are continuously produced from the sacrificial electrode due to the applied external direct current power source and works on the oxidative and reductive principle (Cho et al., 2010). The direct current provided from the electrode neutralized the ionic species present in the wastewater as well as produced metal ions. This neutralization of particles reduced the electrostatic inter particles repulsion sufficiently so that the van der Waals attraction predominates and cause coagulation (Siringi, 2012). The flocs are formed by a coagulation process, which creates a sludge blanket that entraps and bridges colloidal particles that have not been completed. During the electrolysis process, the applied voltage and current can continuously be monitored by digital multi-meter or voltmeter and ammeter respectively.

2.9.2. Brief description of electrolysis mechanism

Coagulation define as the overall process of particle destabilization, transportation and aggregation. Depending on size of the particle, the flocculation process undergo perkinetics (Brownian diffusion), orthokinetics (Shear) and differential settling (gravitational) mechanisms.

It generally accept that coagulation is brought about primarily by the reduction of the net surface charge to a point where the colloidal particles, previously stabilized by electrostatic repulsion, can approach closely enough for van der Waal's forces to hold them together and allow aggregation. The reduction of the surface charge is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte having opposite charge. In the electrolysis process, the coagulant generate in situ by electrolytic oxidation of an appropriate anode material. In this process, charge ionic species remove from wastewater by allowing it to react with (i) an ions having opposite charge, or (ii) flocs of metallic hydroxides generated within the effluent (Mollah et al., 2001).

In electrolysis, electro-flotation, electro-oxidation and electro-coagulation occur simultaneously. Particles aggregate by following at least one or a combination of any of the above-mentioned mechanisms, which are also enhanced by continuous mixing. In electro-flotation, the scum layer usually forms at the water surface. In electro-oxidation, the organics compound present in the water were oxidized as simple carbon containing compounds or carbon dioxide due to breakage of bond between carbon and carbon in most of the cases. In electrolysis, metal ions continuously produce from the sacrificial electrode by direct current. Before electrolysis, the particles suspend because of repulsive force between the charges particles present in the wastewater. However, in electrocoagulation process, the released metal ions contain positive charged particles which react with negatively charge suspended particles and neutralize it, encouraging destabilization of the particle and enhanced flocculation. The collided particle flocs settle down due to gravitational force. Some of the anode and cathode reaction mechanism that take place in the electrode are presented below (El-Shazly et al., 2013; Lucas & Peres, 2009; Sangal et al., 2013):

At Aluminum (Al-Al) electrode:

$$Al\ (s) \rightarrow Al^{3+}\ (aq) + 3e^{-}\ (\text{at anode}) \qquad (2.5)$$

$$3H_2O\ (l) + 3e^- \rightarrow 3/2\ H_2\ (g) + 3OH^-\ (aq)\ \text{(at cathode)} \tag{2.6}$$

$$Al^{3+}\ (aq) + 3OH^-\ (aq) \rightarrow Al(OH)_3\ (s)\ \text{(overall reaction)} \tag{2.7}$$

The aluminum hydroxide flocs have large surface area and adsorb, trap or polymerize colloidal particles and can remove from the aqueous solution. Aluminum hydroxide is also an important adsorbent of organic and inorganic ions, molecules and colloidal particles (Rodriguez et al., 2007).

At Iron (Fe-Fe) electrode:

$$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-\ \text{(at anode)} \tag{2.8}$$

$$2H_2O\ (l) + 2e- \rightarrow H_2\ (g) + 2OH^-\ (aq)\ \text{(at cathode)} \tag{2.9}$$

$$Fe(s) + 2H_2O\ (l) \rightarrow Fe\ (OH)_2\ (s) + H_2\ (g)\ \text{(overall reaction) and/ or} \tag{2.10}$$

$$4Fe(s) + 10H_2O\ (l) + O_2\ (g) \rightarrow 4Fe\ (OH)_3\ (s) + 4H_2\ (g)\ \text{(overall reaction)} \tag{2.11}$$

The liberated Fe^{2+} and OH^- ions react with various monomeric or polymeric iron hydrolyzed species and adsorb pollutant present in the wastewater and to form bigger size flocs and get settle down. In hybrid (Al-Fe) electrode, both the Al-Al and Fe-Fe electrode reaction mechanism may occur during electrolysis.

2.9.2.1. Total Phosphorus reduction mechanism

During electrolysis, hydroxide ions liberated from the cathode react with soluble phosphate containing materials and liberate phosphate ions. The phosphate ions react with the metal ions and produce metal phosphates such as aluminum phosphate or iron phosphate by covalent bonds in the anode. The aluminum or iron phosphates are insoluble in water and settle to the bottom or attract and absorb micro-colloidal particles. Thus, the absorbed micro-colloidal particles form flocs, which settle to the bottom and help decrease the amount of TP from the solution (Dinh-Duc et al., 2014; Inan & Alaydin, 2014).

$$Al\ (s) \rightarrow Al^{3+}\ (aq) + 3e^{-}\ (\text{at anode}) \quad (2.12)$$

$$3H_2O\ (l) + 3e^{-} \rightarrow 3/2\ H_2\ (g) + 3OH^{-}\ (aq)\ (\text{at cathode}) \quad (2.13)$$

$$H_3PO_4\ (aq) + 3OH^{-}\ (aq) \rightarrow 3H_2O\ (l) + PO_4^{3-}\ (aq) \quad (2.14)$$

$$Al^{3+}\ (aq) + PO_4^{3-}\ (aq) \rightarrow AlPO_4\ (s) \quad (2.15)$$

$$Al\ (s) + H_3PO_4\ (aq) \rightarrow AlPO_4\ (s) + 3/2\ H_2\ (g)\ (\text{overall reaction}) \quad (2.16)$$

2.9.2.2. Total Nitrogen reduction mechanism

According to the EPA, TN is the sum of TKN (NH_4-N and organic nitrogen) and NO_2-N+NO_3-N. Therefore, when addressing a TN reduction mechanism by an electrolysis process, it is better to describe all forms of nitrogen reduction mechanisms individually.

The NO_2-N+NO_3-N present in the wastewater is reduced by a chemical denitrification process with the help of metal electrodes such as aluminum or iron during the electrolysis process. The overall denitrification process during electrolysis process is given below (Emamjomeh & Sivakumar, 2009):

$$3NO_3^{-}\ (aq) + 6Al\ (s) + 12H_2O\ (l) \rightarrow 3NH_3\ (g) + N_{2\ (g)}\ (g) + 6Al\ (OH)_3\ (s) + 3OH^{-}\ (aq) \quad (2.17)$$

$$3NO_3^{-}\ (aq) + 6Fe\ (s) + 12H_2O\ (l) \rightarrow 3NH_3\ (g) + N_2\ (g) + 6Fe\ (OH)_3\ (s) + 3OH^{-}\ (aq) \quad (2.18)$$

The NO_2-N+NO_3-N present in the wastewater is removed in the form of nitrogen and ammonia from the wastewater during electrolysis by denitrification process.

Similarly, NH_4-N present in the wastewater is removed by an ammonia stripping method that occurs in the cathode with the help of the hydrogen electroflotation process. Ammonia is also removed by electro oxidation at the anode (Kabuk et al., 2014). The ammonia strip method is enhanced by higher pH (>8), higher temperature (>50 °C) and high airflow rate (Emamjomeh & Sivakumar, 2009; Ilhan et al., 2008). The overall reaction during ammonia stripping method is as follows (Eq. 2.19):

$$NH_4^+ \text{ (aq)} + OH^- \text{ (aq)} \rightarrow NH_3 \text{ (g)} + H_2O \text{ (l)} \tag{2.19}$$

TKN is the sum of organically bound nitrogen and NH_4-N. NH_4-N is removed by the ammonium stripping method as mentioned above (Eq. 2.19) and the organically bound nitrogen is removed by the electrolysis method. The organic nitrogen present in the solution is followed through the electrolysis process as follows (Yun et al., 2014):

$$H_2O \text{ (l)} \rightarrow H^+ \text{ (aq)} + OH^- \text{ (aq)} \tag{2.20}$$

$$\text{Metal (s)} + nOH^- \text{ (aq)} + \text{Organics(aq)} + O_2\text{(g)} \rightarrow \text{Oxidized Organics-Metal (OH) } n\downarrow \text{ (s)} + ne^- \tag{2.21}$$

$$H^+ \text{ (aq)} + e^- \rightarrow H_2 \text{ (g)} \tag{2.22}$$

Therefore, in electrolysis, all types of nitrogen are reduced by a different process and its effect is reflected significantly in TN reduction.

2.9.2.3. Chemical Oxygen Demand (COD) reduction mechanism

COD is measured by the amount of the oxygen needed for the chemical oxidation of inorganic and organic matter present in wastewater. Compounds that contribute to COD are biodegradable organic compounds, non-biodegradable compounds and inorganic oxidizable compounds.

According to Yun et al. (2014), the reduction of organic compounds is occurred by the electrolytic oxidation and electrolysis process. In electrolytic oxidation process, organic compounds are converted into the carbon dioxides gas by complete oxidation process.

$$2H_2O \text{ (l)} \rightarrow 4H^+ \text{ (aq)} + O_2 \text{ (g)} + 4e^- \tag{2.23}$$

$$OH^- \text{ (aq)} \rightarrow 2H_2O \text{ (l)} + O_2 \text{ (g)} + 4e^- \tag{2.24}$$

$$\text{Organics (s)} + O_2\text{ (g)} \rightarrow H_2O\text{ (l)} + CO_2\text{ (g)} \qquad (2.25)$$

Similarly, during electrolysis, water molecules are dissociated in to H^+ and OH^- ions. The combination of metal ions such as Al^{3+} or Fe^{2+} or Fe^{3+} and highly reactive OH^- are responsible for the flocculation/coagulation agent to remove the suspended solid. During COD reduction, the organic or inorganic compounds presented in the feedlot runoff react with the metal hydroxide and produced an insoluble compound (Eqs. 2.20 to 2.22). The soluble COD compound formed during electrolysis does not help for the COD reduction. The COD reduction is also promoted by upward flow of hydrogen gas which is produced during electrolysis process in cathode (Ali & Yaakob, 2012; Moreno-Casillas et al., 2007).

2.9.3. Factors influencing the electrolysis and electrode selection process

Pollutants present in wastewater undergo oxidation and reduction reactions during electrolysis. The rate of electrolysis depends on various factors such as electrode material, effective surface area of electrodes, ionic concentration, electrodes surface geometry, current density, space between electrodes, duration of electrolysis, temperature, electrical conductivity, pH of wastewater, etc. (Bensadok et al., 2011; Inan & Alaydin, 2014; Kushwaha et al., 2010; Yavuz et al., 2011).

Different electrodes have different oxidation potentials (Al^{3+} to Al is -1.66 V, Fe^{2+} to Fe is -0.44 V and Fe^{3+} to Fe^{2+} is -0.771 V). Therefore, the same applied potential between the electrodes made from different materials would have different rates of ionization capacity and rate of redox reaction, which ultimately affect the pollutant reduction capacity of wastewater. Kobya et al. (2006) analyzed potato chips industrial wastewater electrolysis using Al and Fe electrodes. They found that COD, turbidity and suspended solid removal were better when using Al electrodes than the Fe electrode. Similarly, Ilhan et al. (2008) used 0.5 L leachate sample treated by Al and Fe electrodes having effective surface area of 45 cm^2 at 0 to 30 V and 0 to 3 A and they found that COD removal by Al electrode was 56% and Fe electrode was 35%. In the same experiment, NH_3-N reduction by Al and Fe electrodes were 14% and 11%, respectively. Asselin et al. (2008), however, used Fe and Al electrodes for treating bilge water for organics removal and they found that COD removal was higher by Fe electrodes than Al electrodes.

EC of wastewater helps to increase electrolysis current flow and decreases resistance of electrolyte or wastewater due to the formation of ions. Generally, salts such as NaCl or $ZnCl_2$ are used to increase EC in wastewater (Bensadok et al., 2011). According to Sengil (2006), the Cl^- present in NaCl or $ZnCl_2$, also produces Cl_2 and OCl^- in addition to increased conductivity. The OCl^- ions itself is a strong oxidant capable of oxidizing organic molecules present in the wastewater.

The distance between the electrodes also affects the electrolysis process. When the distance between the electrodes increases at constant voltage, the resistance between the electrodes increases and current passing through the electrodes decreases. The decreasing current leads to decreasing formation of ions and pollutant removal efficiency. Dalvand et al. (2011) used an aluminum electrode at 20 V potential and kept the electrode distance from 1 to 3 cm apart, the dye removal efficiency decreased from 98.59% and 90.43% at 30 minute. Similarly, surface area, surface geometry and current density are interrelated and affect the electrolysis process. The ions are provided from the effective surface area of the electrodes and undergo deterioration. From the literature, cylindrical electrodes consumed less energy and produced a greater number of metal electrode ions than other shapes of electrodes due to the uniform electrical charge distribution on the surface (Mandal et al., 2012).

The initial pH of the wastewater also affects the electrolysis process of pollutions. When the initial pH of the electrolyte or wastewater are changed, the formation of iron or aluminum hydroxide and polymeric species are different. pH plays a vital role during electrolysis (Bensadok et al., 2011; Moreno-Casillas et al., 2007; Şengil, 2006).

Initial pollutant concentration also influences the percent reduction of pollutants during electrolysis. The removal of pollutant, specifically COD, is due to the adsorption of pollutant by metallic hydroxide flocs during electrolysis. However, the adsorption capacity of flocs is limited, i.e., increased pollutant concentrations have insufficient amount of flocs for adsorbing all the pollutant molecules which affects pollutant removal efficiency.

The electrolysis operation involves two main types of costs: energy and electrode costs (Dalvand et al., 2011). Electrode selection also depends on the cost of electrodes. Platinum or titanium electrodes can be very useful for pollution or nutrient reduction, but are not used frequently due to their cost. Therefore, Fe or Al electrodes are used extensively at field scale because they are economical, readily available and proven effective (Chaturvedi, 2013). Additionally, Fe and Al electrodes produce low concentrations of Al or Fe hydroxide in wastewater, and are nontoxic (Cerqueira et al., 2011).

CHAPTER 3. MATERIALS AND METHODS

3.1. Background

Feedlot runoff samples were collected from the Beef Research Centre at North Dakota State University, Fargo, North Dakota, US. Two treatment approaches were applied for remediation of feedlot nutrients runoff,   hydroponic treatment and an electrolysis process. Two experiments were conducted at different times of the year and the same runoff samples were not used but the origin of runoff samples were same. This study is a relative comparison of initial nutrient concentration with final nutrient concentration of feedlot runoff. For both experiments, the collected runoff samples were stored at 4 °C and analyzed at room temperature (25±2 °C).

3.2. Hydroponic experiment

3.2.1. Runoff sample collection and preparation for hydroponic experiment

The hydroponic experiments were conducted in two batches. The first batch was conducted using runoff stored in a runoff retention pond of feedlot. The second batch was conducted using runoff collected immediatel pen drainage of the same feedlot by automatic runoff sampler (ISCO sampler). Undiluted, 1:1, and 1:2 dilution series of runoff sample were prepared from the feedlot runoff sample with reverse osmosis (RO) water for the first batch. Samples were stored in containers and fed into small experimental units as needed. From first batch, it was observed that the plants could tolerate undiluted runoff water. Therefore, only undiluted samples were carried out in second batch.

3.2.2. Hoagland solution preparation for hydroponic experiment

The Hoagland solution was prepared using chemical compounds in the laboratory mixing with RO water and store in container. The use of chemicals and its weight was calculated based on nutrient requirement for the plants in the hydroponic culture following modified Hoagland solution making procedure (Hoagland & Arnon, 1938; Hoagland & Arnon, 1950; Jeong & Lee, 1996). These solutions were used to compare plants growth and nutrient uptake under actual feedlot runoff and ideal nutrients containing control solution.

Table 3.1 represents the chemical compounds used in preparing the Hoagland solution for macronutrients for plant's optimum growth in hydroponic condition. Similarly, Table 3.2 representing the chemical compound used in preparing the Hoagland solution for micronutrients for plant's optimum growth in hydroponic condition.

Table 3.1. The amount of chemical compounds used while prepared macronutrients in solution.

S.N	Chemicals	Molecular Formula	Concentration (gL^{-1})
1	Calcium nitrate	$Ca(NO_3)_2.4H2O$ (MW = 236.15)	0.590
2	Potassium nitrate	KNO_3 (MW = 101.10)	0.404
3	Magnesium sulfate	$MgSO_4.7H_2O$ (MW = 246.47)	0.245
4	Ammonium phosphate monobasic	$NH_4H_2PO_4$ (MW = 115.03)	0.230

Table 3.2. The amount of chemicals used while prepared micronutrients in stock solution.

S.N	Chemicals	Molecular Formula	Concentration (gL^{-1})
1	Ferrous sulfate	$FeSO_4$ 7 H_2O (MW = 278.01)	0.00228
2	Manganese sulfate	$MnSO_4.H_2O$ (MW = 169.02)	0.00169
3	Zinc Sulfate	$ZnSO_4$ 7 H_2O (MW = 287.55)	0.00115
4	Cupric Sulfate	Cu SO_4 5 H_2O (MW = 249.68)	0.000125
5	Sodium Molybdate	Na_2Mo O_42H_2O (MW = 241.95)	0.000121
6	Boric acid	H_3BO_3 (MW = 61.83)	0.00123

3.2.3. Experimental design and material used in hydroponic experiment

Greenhouse experiments were conducted in a completely randomized design (CRD) in three replicates. In the first batch, the feedlot runoff in three dilutions (undiluted, 1:1, and 1:2) with RO water was used. The Hoagland solution was prepared for a separate experiment units with three types of plants in three replicates. The first batch has 36 experimental units (4 treatments × 3 plant types × 3 replicates) set-up with the undiluted runoff, 1:1 and 1:2 diluted runoff, and Hoagland solution. Additionally, three buckets of RO water without plants were set-up to measure evaporation rate of greenhouse.

No significance differences in net plants biomass between plants seeded in undiluted and diluted runoff (1:1 and 1:2) in the first batch. In the second batch experiment was conducted using only undiluted runoff and Hoagland solution separately. Therefore, in the second batch of experiment only 18 experimental units (2 treatments × 3 plants type × 3 replications) were used. Same as before, three experimental units were also prepared using 3 bucket of RO water without plants to measure evaporation rate during the experimental period. Thus, in total 21 experimental units were used.

Greenhouse temperature was measured daily and photo synthetically active radiation (PAR) was measured by a LI-250A Light Meter. External day length, solar intensity and temperature data was provided by the North Dakota agricultural weather network (NDAWN).

Buckets (11.4 L rectangular plastic, 28 cm width, 32 cm length and 14 cm depth) were used as hydroponic containers in both the experiments. 10 L feedlot runoff or Hoagland solution was used in each experiment unit. Water hyacinth and water lettuce plants were grouped together according to equivalent size and weight before starting the experiment. Four water hyacinths or water lettuce plants were drained, weighed, and used for seeding in each buckets. Sorghum seedlings were prepared by germinating seeds in rock wool in plastic plant propagation tray in the greenhouse. After 10 days of seedling germination, a predetermined number of sorghum plants (56 seedlings in first batch and 32 seedlings in second batch) were transplanted into runoff and Hoagland solution using thermo coal as supporting medium in each bucket. Sorghum plants spaced 0.045 m in the first experiment. Plants to plant and row to row spacing was 0.045 m x 0.09 m in the second experiment. Therefore, numbers of sorghum seedlings used in the first batch and second batch were 56 and 32 per bucket, respectively. In both batches, dissolve oxygen from the central air compressor of the greenhouse, continuously supplied to the bucket in mist form using a tygon tube (3 mm ID; at the rate 0.2 L per minute) attached with a stone diffuser.

Figure 3.1. Set up for hydroponic experiment inside the greenhouse.

3.2.4. Water sample collection and analysis from the hydroponic experiment

Evaporation and evapotranspiration rate of each bucket was determined by measuring the RO water added to compensate the initial level of the RO water without plants, and runoff and Hoagland solution buckets with plants, respectively. RO water was added to each bucket one hour before water sample collection and collected weekly. EC and pH were measured using a handheld EC and pH meter (YSI Pro Plus, YSI Inc., Ohio, USA) on the same day of sample collection. Collected samples were stored at 4 °C for later nutrient analysis.

Total solids were analyzed using the standard method (APHA 2005). Unfiltered samples were poured into tared crucibles and oven dried at 105 °C for 24 h and weighed after subtracting initial weight of the crucible.

Nutrients in the samples (OP, TP, NH_4-N, NO_3-N+NO_2-N, TKN, and K) were measured using Lachet QuickChem (Lachat Instruments, Loveland, CO) following the procedure summarized in Table 3.3. Before analyzing Ortho-P, NH_4-N, and NO_3-N, water samples were filtered via pressure filtration using 0.45 micron mixed cellulose ester filter (EZ-Pak membrane Filter, Cat. Num. EZHAWG474). For quality assurance and quality control (QAQC) in the QuickChem analysis method, calibration standards and blanks were analyzed at every ten samples. During analysis, out of range samples were diluted, reanalyzed and reported with the dilution factor.

Table 3.3. Method/protocol used to analyze the Hoagland and feedlot runoff samples from hydroponic experiments.

Parameter (mgL^{-1})	Methods /protocol used/ Measurement range
OP[a]	QuickChem Method 10-115-01-1-O (Lachat Instruments, Loveland, CO) Equivalent to EPA 365.1 method; 0-20 mgL^{-1}
NH_3-N[a]	QuickChem Method 10-107-06-1-J (Lachat Instruments, Loveland, CO) Equivalent to EPA 353.2 method; 0-20 mgL^{-1}
NO_2 + NO_3-N[a]	QuickChem Method 10-107-04-1-R (Lachat Instruments, Loveland, CO) Equivalent to EPA 350.1 method; 0-20 mgL^{-1}
K[b]	Hach Method 8049 (Tetraphenylborate); 0-7 mgL^{-1}
TP[b]	Hach Method 10127 (Molybdovanadate Method with Acid Persulfate Digested); 1-100 mgL^{-1}
TKN	APHA 2005 4500-N C (Semi Micro Kjeldahl Method)
TN[b]	Hach Method 10072 (Acid Persulfate Digestion); 2 -150 mg L^{-1}

a Equivalent EPA methods
b USEPA approved for reporting

The fresh plants' biomass were calculated after they were washed, cleaned, and soaked 10 minutes with dried paper towel as described by Itoh andBarber (1983). Water content of plants (dry weight) was determined using oven drying method, dried at 105 °C for 24 h or until a constant weight was reached. Plant chlorophyll content was measured using a Soil Plant Analysis Development (SPAD) chlorophyll meter. Conclusion of the experiments were based on visual inspection as well as SPAD meter readings as the leaves or whole plant changed from dark green to yellowish green.

Concentration of minerals such as calcium, magnesium, sulfur, zinc, manganese, copper, molybdenum, boron, and iron (Ca, Mg, S, Zn, Mn, Cu, Mo, B, and Fe) in feedlot runoff and plant tissue (before and after experiment) were measured by Inductively Coupled Plasma Spectroscopy (ICP). ICP used 2010-11-15 Standard Method in the Wet Ecosystem Lab at North Dakota State University.

3.2.5. Removal efficiency of nutrients in hydroponic treatment

The net plant biomass was calculated using the following formula:

$$\text{Net plant biomass} = \text{Final weight of plant} - \text{Initial weight of plant} \tag{26}$$

The percentage of nutrient removal was calculated using the following formula:

$$\%\ \text{removal efficiency of parameter} = \frac{\text{Initial concentration } (\mathrm{C_i}) - \text{final concentration } (\mathrm{C_f})}{\text{Initial concentration } (\mathrm{C_i})} \times 100\% \tag{27}$$

3.3. Electrolysis process

3.3.1. Feedlot runoff collection, storage and sample collection

Feedlot runoff samples were collected from the Beef Research Centre at North Dakota State University, Fargo, North Dakota, US. Collected sample was stored in 20 L bucket at 4 °C and analyzed at room temperature (25±2 °C). During electrolysis, a 500 mL sample placed into a 550 mL beaker. Initial pH and EC were measured with a handheld pH and EC meter (YSI Pro Plus, YSI Inc., Ohio, US). TS measurements were before starting electrolysis. At predetermined times (0, 1, 2, 3, 5, 8, 10, 20 and 30 minutes of electrolysis), 10 mL of treated sample was collected and pipetted in test tubes and left them for 24 h at room temperature for settlement and nutrient analysis was done later on from the supernatant. In this experiment, three potentials applied for three electrodes with three replicates. A total of 243 (3 × 3 × 3 × 9) samples were collected during the electrolysis study.

3.3.2. Description of electrolysis operation systems

Parallel plates with identical dimensions of aluminum (Al-Al), iron (Fe-Fe) and hybrid (Al-Fe) electrodes pair were used in electrolysis process. A direct current (DC) was applied through the single anode and cathode using a DC power source equipped with digital ammeter and voltmeter (BK precision 1621A DC regulated power supply equipment) and maintained at 5 V, 10 V or 15 V electrical potential (Fig. 1). The submerged portion of electrode was 90 mm × 25 mm × 1.5 mm ($h \times b \times t$) and the space between the electrodes was kept constant at 8 mm an effective area 4807.5 mm^2. Corresponding current measured according to applied potentials for each treatment condition to determine electrical energy consumption and pollutant reduction capacity of each type of electrode. During electrode polarity change, both electrodes can be used equally (especially the hybrid electrode pair) hence in this experiment the polarity of electrodes was altered manually to adjust current through the electrodes. Sample was mixed continuously with a 30 mm magnetic stirrer at 200 to 300 rpm. After electrolysis, the sludge was collected and filtered using 0.45 micron mixed cellulose ester filter (EZ-Pak membrane Filter, Cat. Num. EZHAWG474) and dried in an oven at 105 °C for the elemental analysis. Electrodes were rinsed with diluted hydrochloric acid (5% v/v) followed with DI water rinse to avoid the electrode passivation due to oxidation and contamination of products.

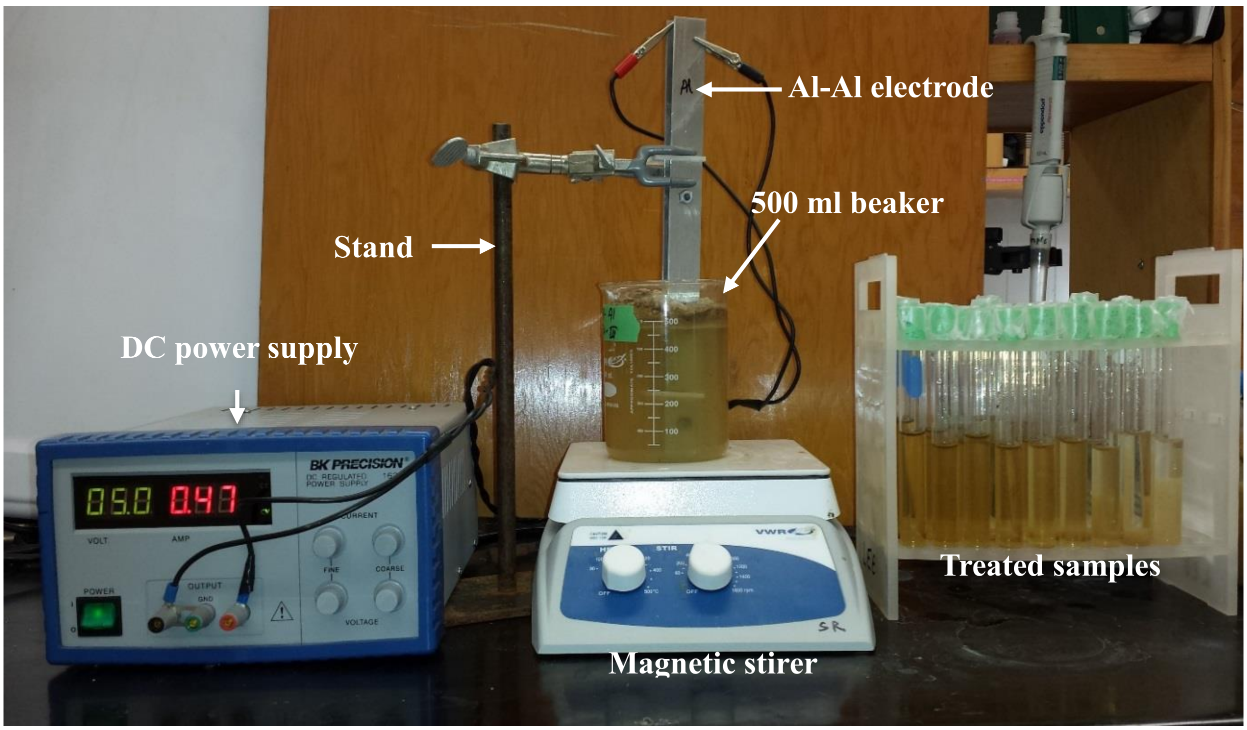

Figure 3.2. Set up for the electrolysis process.

3.3.3. Sample and data analysis

The Hach Method 10127 (Molybdovanadate Method with Acid Persulfate Digested, 1-100 mgL^{-1}) was used for TP analysis. The Hach Method 10072 (Persulfate digestion method 2-250 mgL^{-1}) was used for TN analysis, and Hach Method 8000 (Reactor digestion method 20-

1500 mgL^{-1}) was used for COD analysis. Mineral concentration in the dried sludge was measured with Inductively Coupled Plasma Spectroscopy (ICP) using a 2010-11-15 Standard Method in the Wet Ecosystem Lab at North Dakota State University.

The mean concentration of pH and EC were compared before and after an electrolysis treatment, TN, COD, and TP results in runoff were compared at each sampling time during electrolysis, as well as with initial concentration. Mean concentration of the pollutants (EC, pH, TP, COD, and TN) and estimated removal efficiencies in each voltage potential and electrode type were compared using Analysis Of Variance (ANOVA). The null hypothesis tested was that mean pollutant concentrations and removal efficiencies among voltage and electrodes were equal. All statistical analysis were done using SAS software version 9.3 using PROC means procedure at 5% level of significance.

3.3.4. Calculation of removal efficiency and specific electrical energy consumption

The removal efficiencies for TN, TP and COD were calculated using Equation (27). The specific electrical energy consumption per unit mass of parameter was calculated using Equation (28) and per unit volume of runoff was calculated using Equation (29) as follows:

$$\text{Specific electrical energy consumption per unit mass of parameter}$$

$$= \frac{\mathrm{V \times I \times t\ (Kwh)}}{\text{mass of parameter reduced(kg)}} \tag{28}$$

Where V= applied potential difference for electrolysis process, voltage

I= current generated in electrolysis process, amperes

t= time of electrolysis process, hours

Specific electrical energy consumption per unit volume

$$= \frac{\mathrm{V \times I \times t \ (Kwh)}}{\mathrm{volume\ of\ runoff\ used\ (m^3\ )}} \tag{29}$$

Where V= applied potential difference for electrolysis process, voltage

I= current generated in electrolysis process, amperes

t= time of electrolysis process, hours

CHAPTER 4. RESULTS AND DISCUSSION OF HYDROPONICS EXPERIMENT

4.1. Background of greenhouse hydroponic experiment

4.1.1. Feedlot runoff and Hoagland solution characteristics

The chemical characteristics analyzed from the undiluted and diluted feedlot runoff and the Hoagland solution in the first and second batches are presented in Tables 4.1 and 4.2, respectively. In general, the concentration of nutrients in feedlot runoff was higher in the second batch than those with the first batch except for NO_3-N+NO_2-N (which was approximately 5 times lower than the first batch). The concentrations of pH was similar between two batches. In contrast, EC and concentrations of TS, TP, OP, TKN, NH_4-N, and K in the second batch feedlot runoff experiment were approximately 5, 4.5, 6, 2, 6, and 14 times higher than those measured in the first batch (collected from runoff retention pond), respectively. The nutrients concentration of Hoagland solution in both batches were similar because of same making procedure. Macronutrient concentrations such as TP, TKN, NH_4-N, NO_3-N+NO_2-N, and K with feedlot runoff were about 11, 1.2, 83, 7, and 2.5 times lower than those with Hoagland solution during the first batch experiment (Table 4.1.). However, in the second batch, TP, TKN, NO_3-N+NO_2-N concentrations with Hoagland solution were approximately 1.75, 2, and 441 times higher than feedlot runoff. In the contrary, K concentrations in second batch feedlot runoff were approximately 6 times higher than K concentrations measured with Hoagland solution (Table 4.2.).

Table. 4.1. Characteristics of initial feedlot runoff samples collected from the feedlot runoff and Hoagland solution used to grow plants hydroponically in the first batch.

Parameters	Feedlot runoff (undiluted)	Feedlot runoff (1:1)	Feedlot runoff (1:2)	Hoagland solution
pH	7.45±0.029	7.51±0.025	7.63±0.080	5.76±0.012
EC (mS cm^{-1})	0.80±0.004	0.48±0.003	0.37±0.005	1.55±0.026
TS (mgL^{-1})	0.75±0.026	0.42±0.009	0.32±0.015	1.07±0.034
TP (mgL^{-1})	16.53±3.691	6.07±1.779	4.23±0.833	175.92±23.880
OP (mgL^{-1})	8.23±1.198	4.47±0.359	2.51±1.051	66.47±5.832
TKN (mgL^{-1})	53.5±2.043	45.93±7.635	40.27±0.231	64.93±8.570
NO_3-N+NO_2-N (mgL^{-1})	1.43± 0.494	1.01±0.836	0.59±0.011	117.64±6.294
NH_4-N (mgL^{-1})	4.26± 0.376	1.91±0.237	1.26±0.026	29.97±1.258
K (mgL^{-1})	57.23±11.662	47.13±11.662	30.60±5.100	144.77±15.428

Table. 4.2. Characteristics of feedlot runoff collected from the feedlot and Hoagland solution used to grow plant hydroponically in the second batch.

Parameters	Feedlot runoff (undiluted)	Hoagland solution
pH	7.97±0.035	6.21±0.038
EC (mS cm^{-1})	3.99±0.031	1.47±0.026
TS (mgL^{-1})	3.41±0.183	0.97±0.577
TP (mgL^{-1})	95.70±11.370	168.17±2.696
OP (mgL^{-1})	13.69±1.48	64.83±4.155
TKN (mgL^{-1})	217.20±22.17	99.87±9.386
NO_3-N+NO_2-N (mgL^{-1})	0.28± 0.006	123.50±1.323
NH_4-N (mgL^{-1})	32.20±0.781	34.05±7.496
K (mgL^{-1})	777.70±26.722	134.67±5.831

4.1.2 Greenhouse environment

The first batch hydroponic experiment was conducted from June -13 to July-4, 2013, with day light duration of 15 hours to 16 hours. The average daily ambient temperature ranged from 25 °C to 29 °C and solar radiation ranged from 1169 µmol s^{-1} m^{-2} to 1243 µmol s^{-1} m^{-2}. Corresponding temperature and solar radiation in the greenhouse ranged from 25 °C to 30 °C and 525 µmol$s^{-1}m^{-2}$ to 610 µmol$s^{-1}m^{-2}$, respectively. The second batch experiment was conducted between 9 September to 14 October, 2013, when day light duration was between 11 hours to 13 hours, The average daily ambient temperature and solar radiation ranged from 6 °C to 18 °C and 346 µmol $s^{-1}m^{-2}$ to 600 µmol $s^{-1}m^{-2}$, respectively. At the same time, greenhouse temperature was varied from 20 °C to 25 °C and solar radiation was varied from 225 µmol$s^{-1}m^{-2}$ to 410 µmol$s^{-1}m^{-2}$. Overall, solar radiation in the first batch experiment was 1.5 times higher than the second batch experiment though the inside greenhouse temperatures were almost same.

4.2. Net plant biomass

Water hyacinth, water lettuce, and sorghum plants grew up well in both batch experiments. However, the water lettuce in the Hoagland solution in the second batch experiment did not grow well, which was probably due to pathogens or disease. The sorghum grew at the highest rate and water lettuce grew at least in both batch experiments (Figs. 4.1 & 4.2). Growth of water hyacinth was in the mid-range. In both batch experiments, plant seeded in the Hoagland solution produced more net plant biomass than plant seeded in the feedlot runoff water (Figs. 4.1 & 4.2). The lower biomass in the feedlot runoff was likely due to lower ammonium, and nitrate and nitrite nitrogen concentration in the feedlot runoff than the Hoagland solution. The net growths of plants in the diluted feedlot runoff were lower than the plants grew in undiluted feedlot runoff water sample (Fig. 4.1). The low net plant biomass in diluted feedlot runoff water was due to the dilution of nutrients present in feedlot runoff water. This demonstrated that, although feedlot runoff might not have the ideal nutrient contents, runoff can use to grow plants and to reduce nutrient runoff.

In both batch experiments, the plants seeded in the Hoagland solution were the reference plants and net plant biomass of the plant was compared with those seeded in feedlot runoff. The net plant biomass grown in the feedlot runoff and Hoagland solution during the first batch of experiments was higher than that grown in the same media during the second batch experiment. However, the first and second batch experiments conducted in 3 weeks and 5 weeks period, respectively (Figs. 4.1 & 4.2). Higher net plant biomass during first batch than the second experiment were mainly due to longer solar day (June-July) coupled with appropriate intensity of photosynthetically active solar radiation. The length of root was longer and brown in color for all plants in the first batch experiment, which seeded in the feedlot runoff as compared to the Hoagland solution (data was not taken).

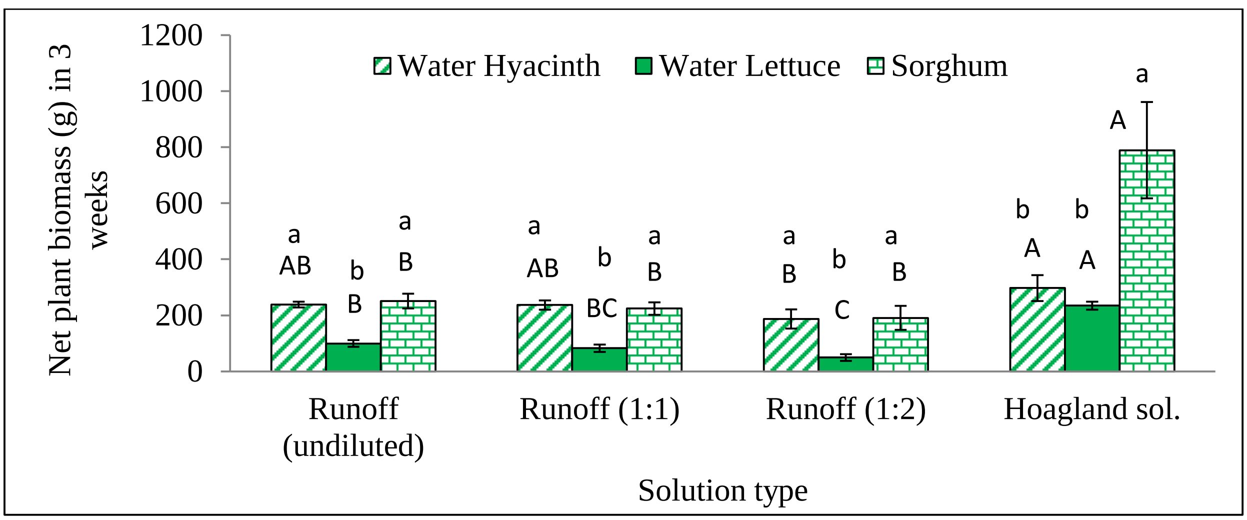

Figure 4.1. Net plant biomass of water hyacinth, water lettuce, and sorghum in the first batch during 3 weeks. Bar with the same capital letter and the same plant type are not significantly different over the experiment period. Similarly, the same small letter for the same runoff type and different plants are not significantly different from each other at p≤0.05.

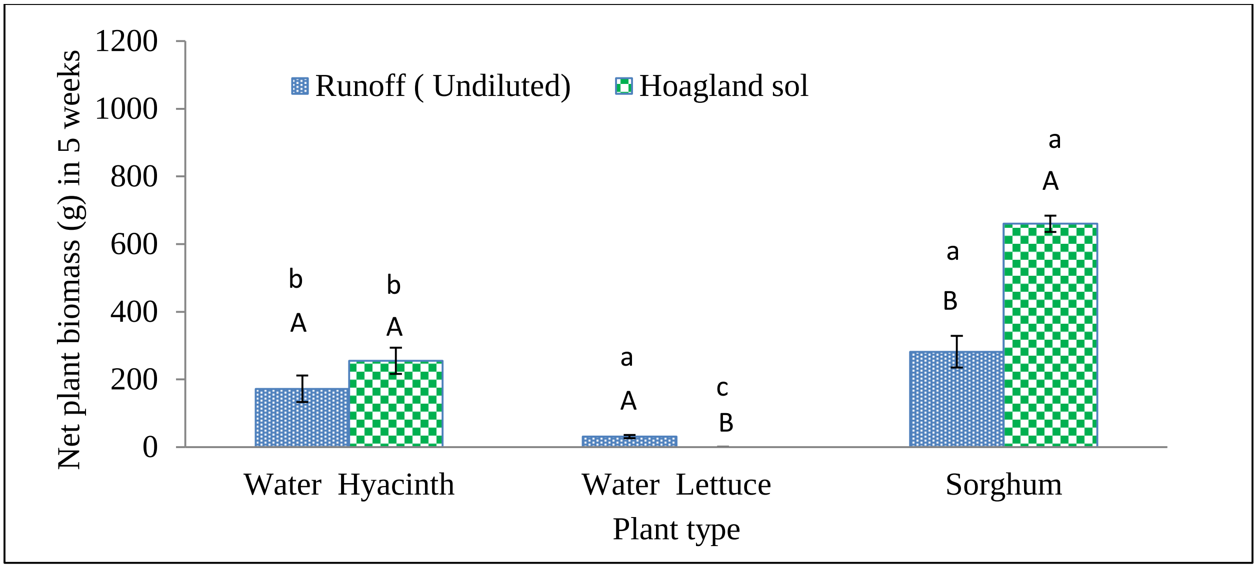

Figure 4.2. Net plant biomass of water hyacinth, water lettuce, and sorghum in the second batch during 5 weeks. Bar with the same capital letter and the same plant type are not significantly different over the experiment period. Similarly, the same small letter for the same runoff type and different plants are not significantly different from each other at $p \leq 0.05$.

4.3. Evapotranspiration (ET)

In the first and second batches, a total of 4.80±.62 and 5.90±0.48 L RO water was evaporated, respectively. In the first batch, sorghum ET rate was significantly higher than the rates for water hyacinth and water lettuce grown in Hoagland solution (Tables 4.3 & 4.4). In contrast, the ET of water hyacinth grown in the feedlot runoff was significantly higher than the rates for sorghum and water lettuce in the first batch ($p<0.05$). Similarly, water hyacinth and water lettuce ET were similar and significantly different from ET of sorghum plants in diluted feedlot runoff sample ($p>0.05$: Table 4.3). In the second batch, all plants showed similar ET in Hoagland solution ($p>0.05$; Table 4.4). In comparision to feedlot runoff, ET for sorghum grown in the were significantly higher than those of water hyacinth and water lettuce ($p<0.05$). In general, ET is influenced by the greenhouse microclimate including solar intensity, air temperature, and vapor pressure differences, and plant physiological parameters including leaf area index. In the first batch, higher solar radiation and higher plant biomass of sorghum in the Hoagland solution and higher plant biomass of water hyacinth in feedlot runoff resulted in higher ET. However, in the second batch higher plant biomass of sorghum in feedlot runoff resulted higher evapotranspiration rate.

Table 4.3. Water added data during 3 weeks of first batch hydroponic experiment.

Parameters	Water Hyacinth(L)	Water Lettuce (L)	Sorghum(L)
Hoagland sol	7.8b±0.85	5.58c±0.58	12.97a±0.64
Runoff (undiluted)	7.67a±0.4	6.13b±0.76	5.07c±0.29
Runoff (1:1)	6.20a±0.20	6.33a±0.15	4.90b±0.10
Runoff (1:2)	6.50a±0.40	6.10ab±0.17	5.37b±0.84

Table 4.4. Water added during 5 weeks of second batch hydroponic experiment.

Parameters	Water Hyacinth (L)	Water Lettuce (L)	Sorghum (L)
Hoagland sol	6.93a±0.25	6.33a±0.57	6.10a±0.66
Runoff (undiluted)	7.07b± 0.15	6.63c±0.15	10.10a±0.26

4.4. pH change over time

The initial pH of feedlot runoff water in first and second batch hydroponic experiments was 7.45 and 7.97, respectively (Figs. 4.4 & 4.8). Similarly, initial pH of the Hoagland solution was 5.76 and 6.21 in the first and second batch experiment, respectively (Figs. 4.3 & 4.7). Thus, feedlot runoff samples were slightly alkaline and the Hoagland solution was slightly acidic in nature. Measured pH levels at each sampling time over the whole experiment period were similar and did not show any noticeable trends for particular plant with feedlot runoff. However, pH of the Hoagland solution seeded with sorghum resulted in either increase in pH or remained the same (data are not shown) (Tarre & Green, 2004). In Hoagland solution, NO_3^- was about 4 times higher than the NH^+ and sorghum plants remarkably uptake NO_3^- . A plant uptaking, one NH^+ or NO_3^- is assumed to release one H^+ or one OH^-, respectively. Therefore, uptaking a higher amount of NO_3^- from the Hoagland solution by sorghum increased the pH value of the Hoagland solution significantly (data are not shown) (Dejaegere et al., 1984; Jeong & Lee, 1996). The fluctuation of pH value of feedlot runoff was likely due to the nitrification process of bacteria (Figs. 4.3 & 4.7).

In first batch, weekly measured pH values were significantly different and showed either increasing or decreasing trends depending on plants grown in feedlot runoff over the experiment period (Figs 4.4, 4.5, & 4.6). Plants grew in feedlot runoff started to show significant pH increments from the second-week of the experiment initiated (Fig. 4.4). Similarly, pH of the feedlot runoff (1:1) increased slightly after the first week of plantation. The final pH concentration measured in feedlot runoff (1:1) was significantly higher than that of initial values for water lettuce ($p<0.05$; Fig. 4.5). There were no significant differences in pH values for water hyacinth and sorghum between initial and final measurement ($p>0.05$). Similarly, there were no significant differences in pH values for water hyacinth and sorghum between initial and final measurement ($p>0.05$) for feedlot runoff (1:2). However, sorghum grown on feedlot runoff (1:2) showed significantly higher pH concentration at the end of the treatment period ($p<0.05$; Fig. 4.6). For the Hoagland solution, the pH value was first decreased and then increased slightly for water hyacinth and water lettuce and were not significantly different from the initial pH. Sorghum plants showed increasing pH in each successive week and shown significantly higher pH values in weeks two and three (Fig. 4.3).

In second batch, pH of feedlot runoff units were significantly different from their initial values (Fig. 4.8). There were no significant differences in pH values for water hyacinth and sorghum between initial and final measurement ($p>0.05$). However, pH values for the water lettuce grown in feedlot runoff was significantly different between initial and final measurement ($p>0.05$). Plants grown in the Hoagland solutions showed wide fluctuations (increasing or decreasing) compared to initial pH values during the course of the 5 week experiment period (Fig. 4.7). The final pH concentration with sorghum grown in the Hoagland solutions was significantly higher than that of initial. In contrast, water hyacinth in feedlot runoff showed significantly lower pH values than initial ($p<0.05$; Fig. 4.7). There were no significant differences in pH values for water lettuce between initial and final measurement ($p>0.05$).

In first batch, pH of Hoagland solution were not significantly different by plant types at the end of experiment. But, it was fluctuating in the first and second week due to plant type (Fig. 4.3). The pH of feedlot runoff seeded with water hyacinth was significantly lower than feedlot runoff seeded with water lettuce and sorghum at final week of experiment, though the pH of feedlot runoff in first and second weeks were not significantly different (Fig. 4.4). Similarly, pH of feedlot runoff (1:1) seeded with water hyacinth was significantly lower than water lettuce and sorghum, and pH of feedlot runoff (1:2) seeded with sorghum was significantly lower than the water hyacinth and water lettuce. In second batch, water hyacinth seeded in the Hoagland solution was the significantly lower, sorghum was significantly higher and water lettuce was in between them (Fig. 4.7). However, the pH of feedlot runoff seeded with sorghum and water hyacinth were not significantly difference, but lower than the water lettuce (Fig. 4.8).

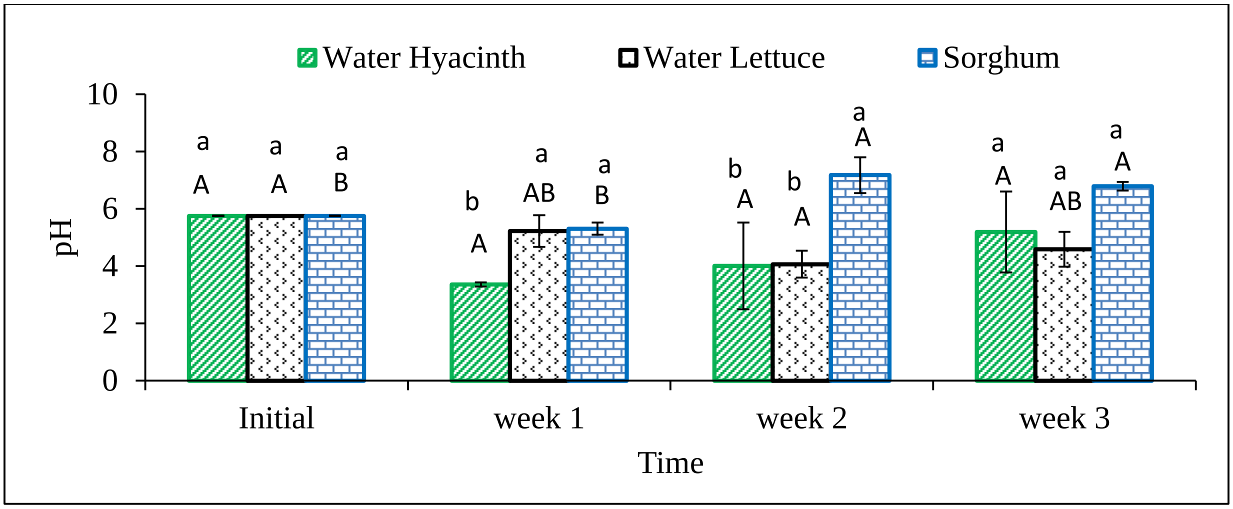

Figure 4.3. pH of the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

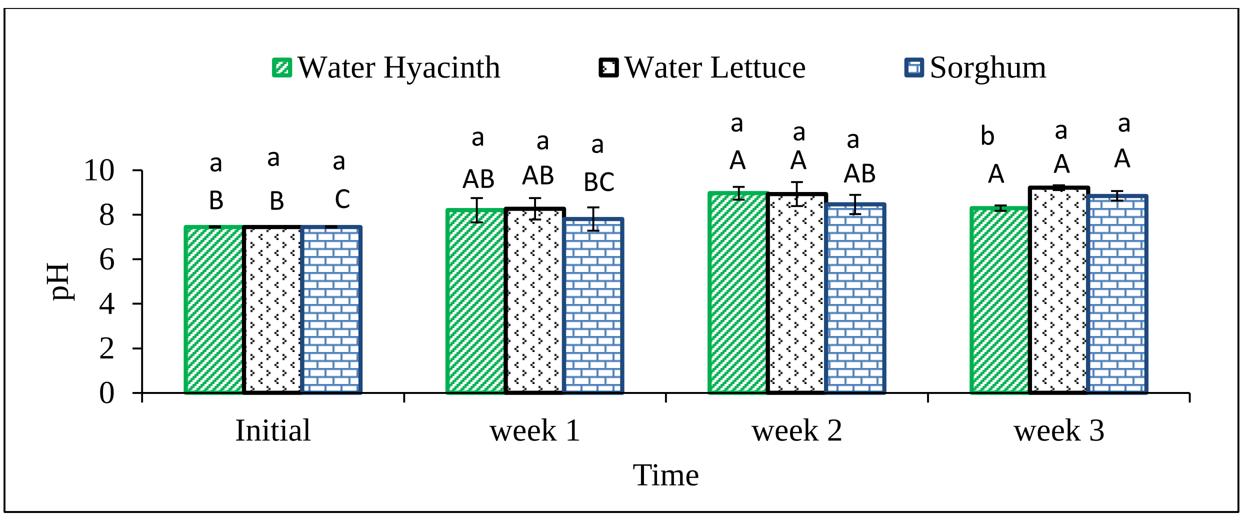

Figure 4.4. pH of the feedlot the runoff (undiluted) sample in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

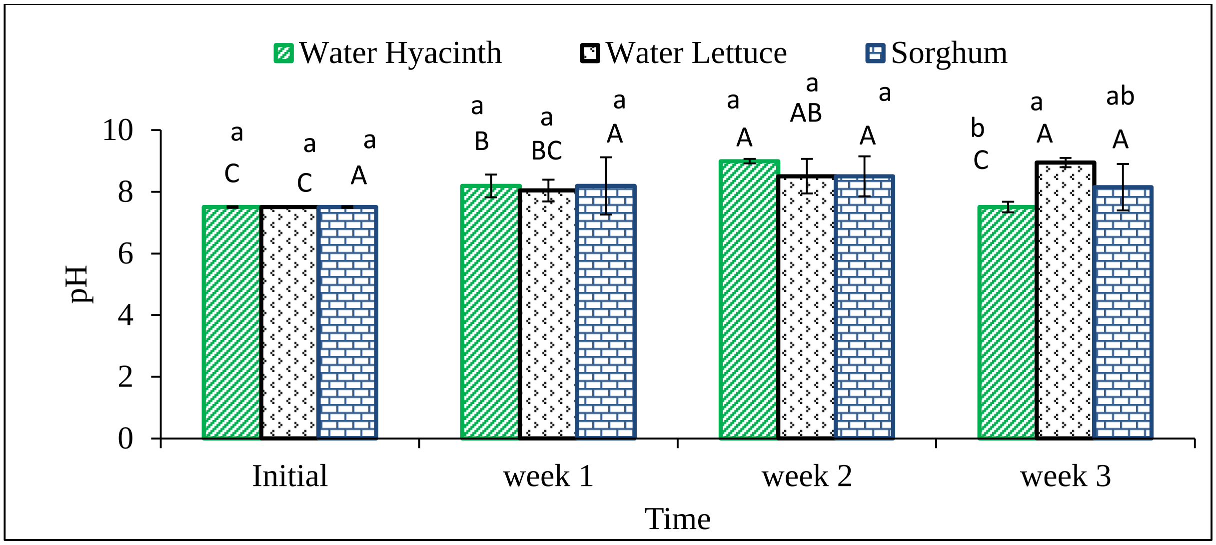

Figure 4.5. pH of the feedlot runoff (1:1) sample in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly,the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

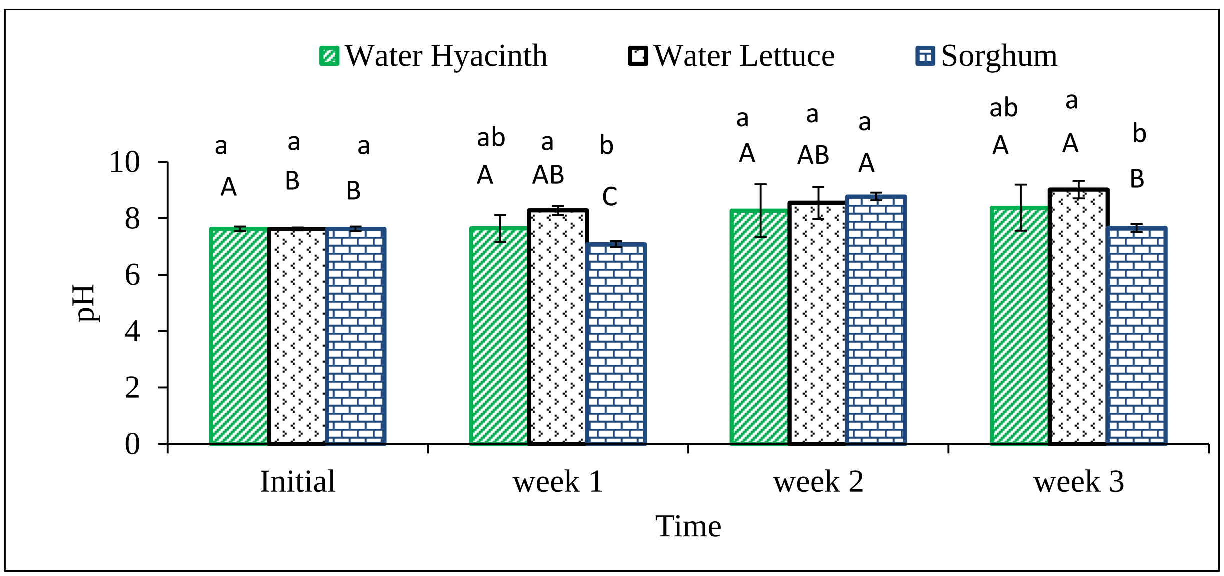

Figure 4.6. pH of the feedlot runoff (1:2) sample in the first batch experiment. Graph with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

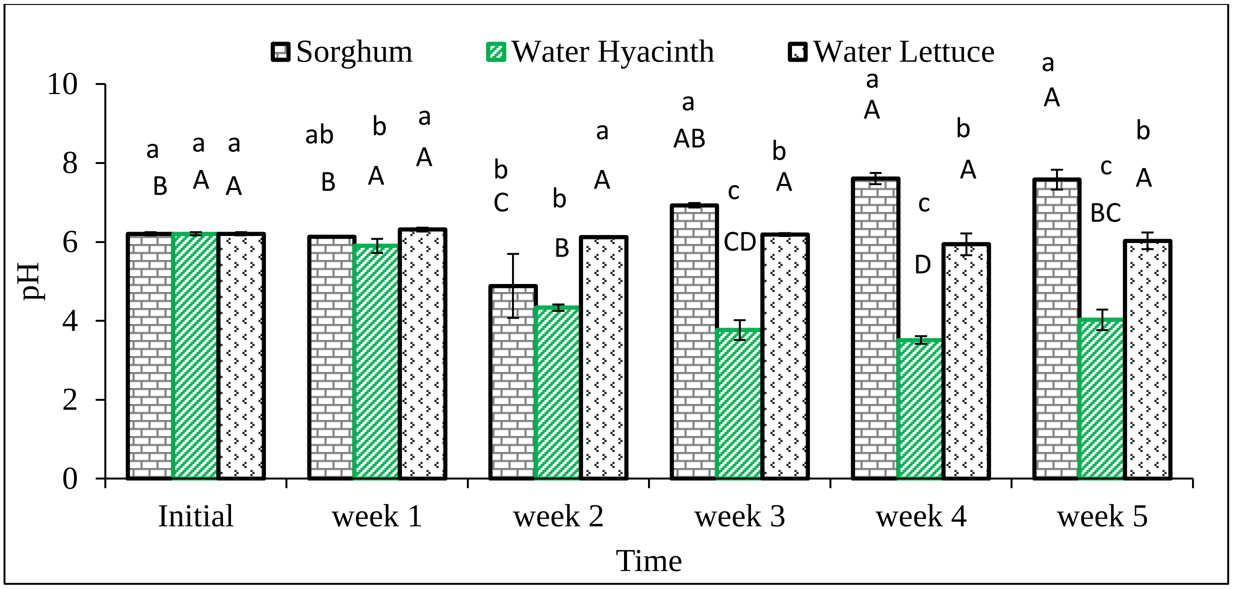

Figure 4.7. pH of the Hoagland solution sample in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

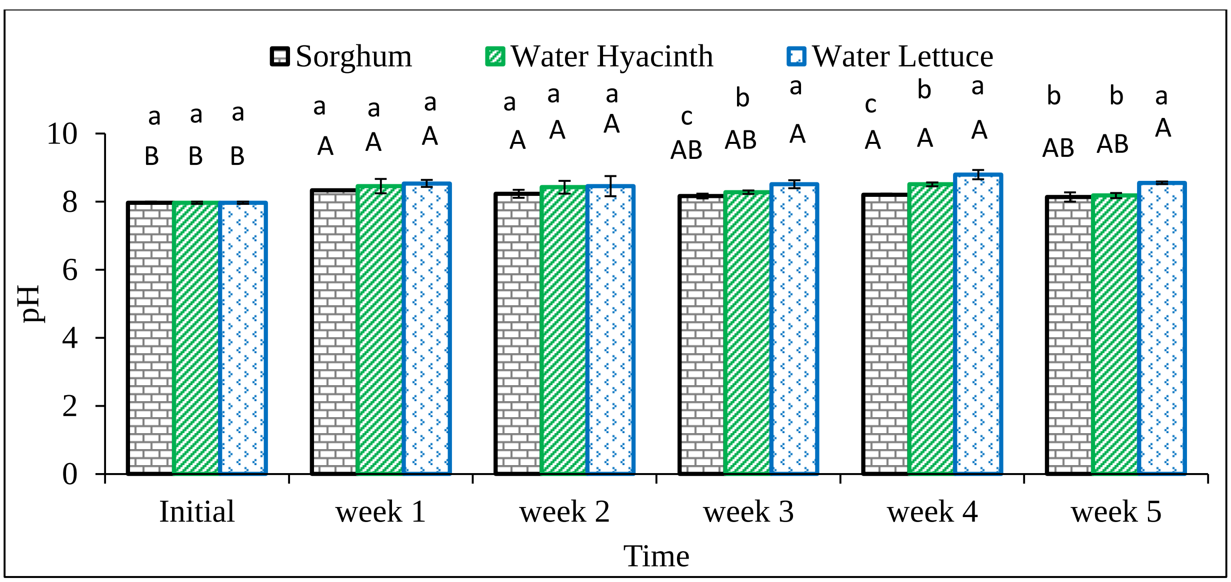

Figure 4.8. pH of the feedlot runoff (undiluted) sample in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

4.5. Electrical Conductivity (EC) reduction

Initial EC was 0.8 $mScm^{-1}$ and 3.99 $mScm^{-1}$ in feedlot runoff in the first and second batch, respectively. The corresponding EC of the Hoagland solutions was 1.55 $mScm^{-1}$ and 1.47 $mScm^{-1}$, respectively. This differences in EC between feedlot runoff were due to sampling locations (at the immediate pen drainage and runoff collection pond) and collection methods (grab vs. automatic sampler), retention time, and rainfall intensity. The plants thrived in all the feedlot runoff and Hoagland solution since the measured EC values for solutions evaluated in this research were below the tolerance limit of the plants tested. The threshold salt tolerance level of the sorghum is 6.8 $mScm^{-1}$ (Tabatabaei & Anagholi, 2012), of water hyacinth is 2.85 $mScm^{-1}$ (Rotella, 2010), and of water lettuce is 2.9 $mScm^{-1}$ (Haller et al., 1974). The corresponding lethal limits of ECs are 12 $mScm^{-1}$, 7.8 $mScm^{-1}$, and 4 $mScm^{-1}$ for sorghum, water hyacinth, and water lettuce, respectively (Gupta et al., 2012; Rani et al., 2012; Rotella, 2010). Therefore, the measured salinity values in the Hoagland solution in both experiments were within the threshold EC level, but the EC values in feedlot runoff in the second batch experiment was higher than the threshold EC value of water hyacinth and water lettuce. Thus, this research demonstrated that water hyacinth and water lettuce could grow within 4 $mScm^{-1}$ salinity level. As plants were grown, water samples were collected at different times. The EC of feedlot runoff and Hoagland solution decreased gradually over the experimental period as shown in the Figures. 4.9 to 4.14. The salinity of the feedlot runoff and the Hoagland solution were reduced continuously due to the uptake of salt ion and nutrient ion form the solution by plants.

In the first batch, all three plants reduced EC significantly after the first week from the feedlot runoff (undiluted) and feedlot runoff (1:1) ($p<0.05$; Figs 4.10 & 4.11). Similarly, in feedlot runoff (1:2), except water lettuce, other two plants started to reduce EC significantly after

2 weeks (Fig. 4.12). In the Hoagland solution, sorghum, water lettuce, and water hyacinth started to reduce EC significantly from the first, second, and third weeks of plantation, respectively (Fig. 4.9). In the second batch, EC of feedlot runoff increased in the first week and reduced significantly after that. EC of sorghum seeded in runoff sample reduced significantly in second, fourth, and fifth weeks than the initial EC value. Similarly, water lettuce grown in runoff samples reduced EC significantly in second week and water lettuce reduced EC significantly in fourth week (Fig. 4.14). In the Hoagland solution, all plants reduced EC. EC of the runoff solution seeded with water lettuce increased significantly in the first and third week. Similarly, for water hyacinth seeded in runoff, the EC of the runoff samples increased significantly in the first week and decreased significantly after third week of plantation, but for the sorghum seeded runoff, the EC reduced significantly since second week and continued until experiment terminated (Fig. 4.13).

In the first batch, water lettuce seeded in the Hoagland solution reduced the most EC and water hyacinth reduced the least amount (Fig. 4.9). Though, EC reduction were not significantly different by plant types in each sampling week in feedlot runoff (Fig. 4.10), water hyacinth reduced significantly greater EC than water lettuce and sorghum from feedlot runoff (1:1) (Fig. 4.11) and water hyacinth significantly reduced EC than water lettuce and sorghum form the feedlot runoff (1:2) (Fig. 4.12). In the second batch, EC reduction by plants form the Hoagland solution were in the order of sorghum, water hyacinth and water lettuce (Fig. 4.13). The EC reduction from the feedlot runoff by sorghum was significantly higher than the water lettuce and water hyacinth from the second week to the end of experiment (Fig. 4.14).

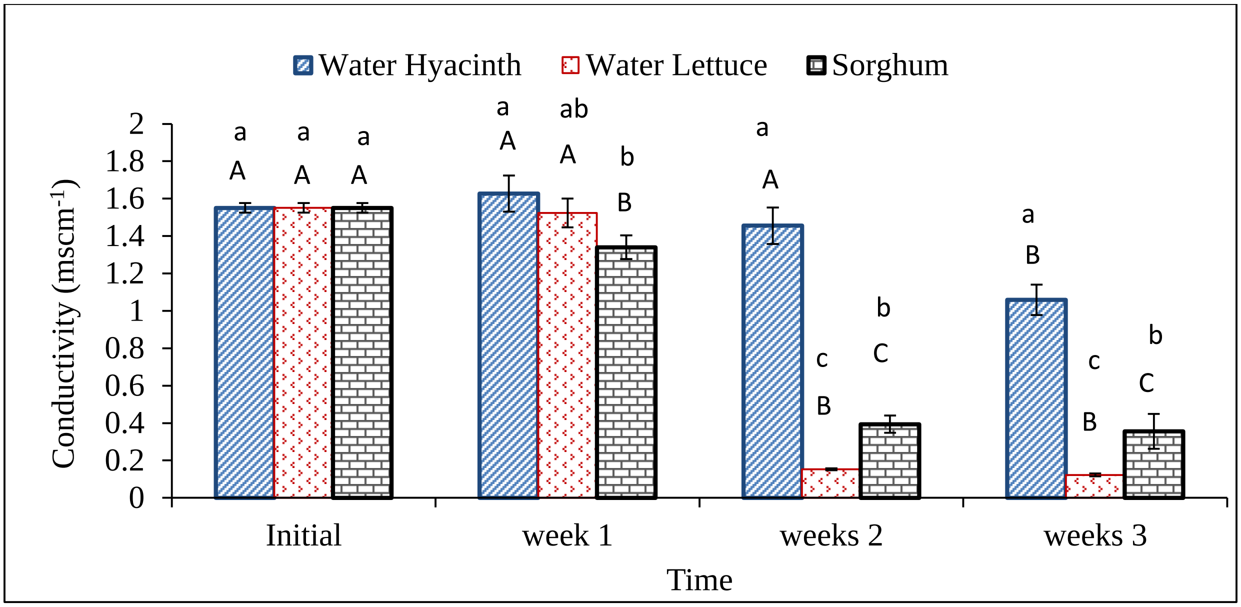

Figure 4.9. Electrical Conductivity (EC) of the Hoagland solution in the first batch experiment. Bar with the same capital letter and same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

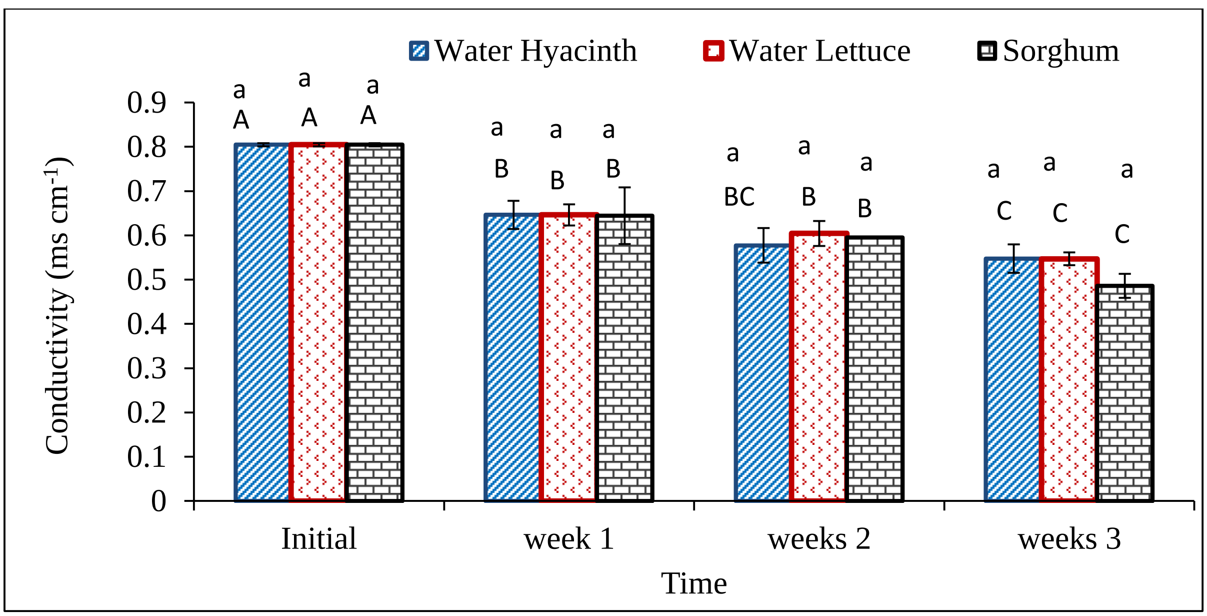

Figure 4.10. Electrical Conductivity of the feedlot runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

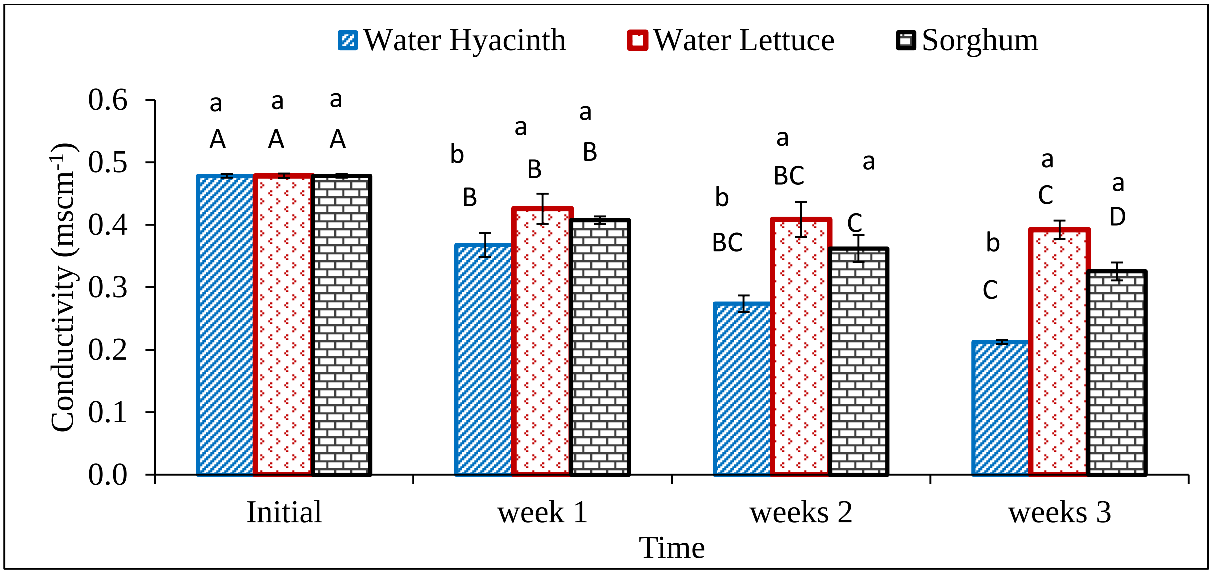

Figure 4.11. Electrical Conductivity of the feedlot runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

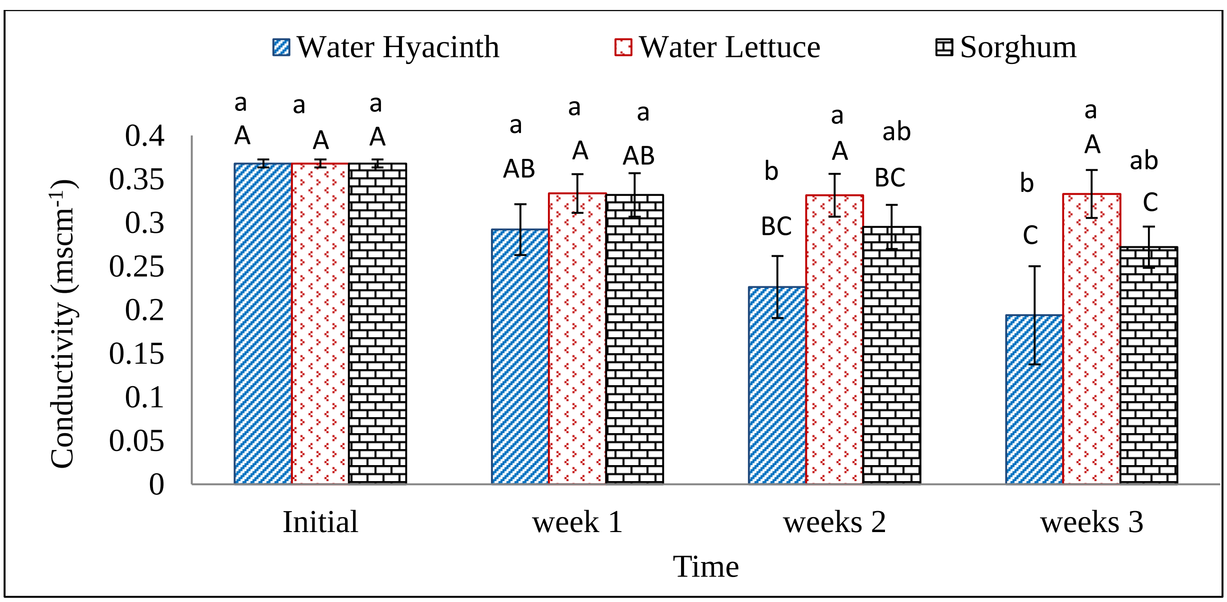

Figure 4.12. Electrical Conductivity of the feedlot runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

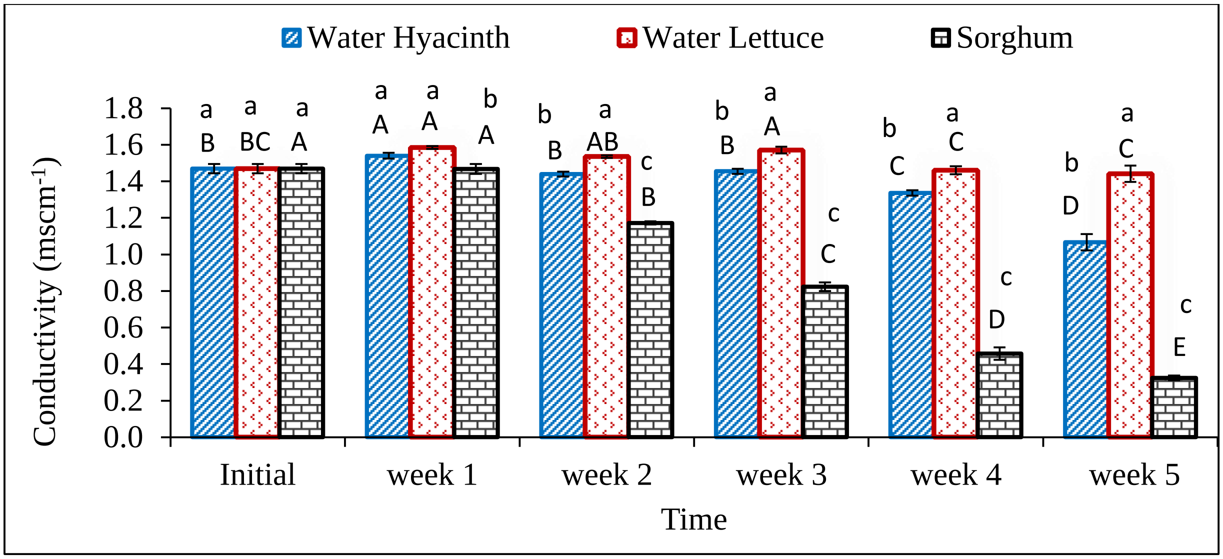

Figure 4.13. Electrical Conductivity of the Hoagland solution in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different with each other at p≤0.05.

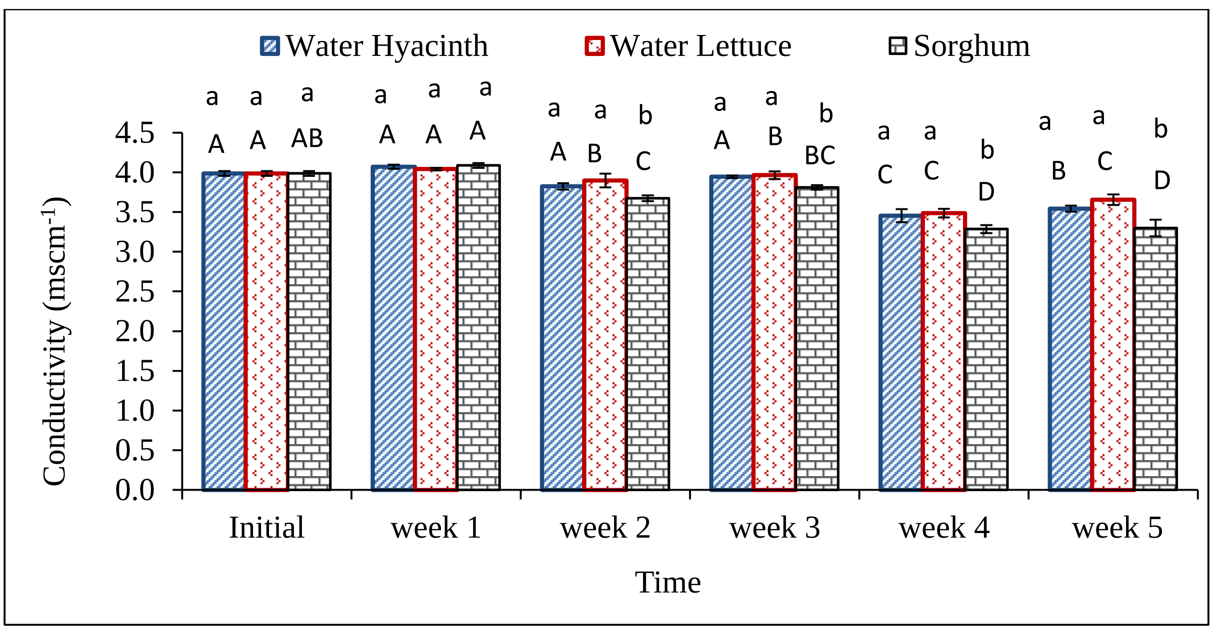

Figure 4.14. Electrical Conductivity of the feedlot runoff (undiluted) in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

4.6. Ammonium Nitrogen reduction

The NH_4-N in first and second batch of feedlot runoff was 4.26 and 32.2 mgL^{-1}, respectively. Similarly, the NH_4-N concentration in Hoagland solution was 29.97 and 34.05 mgL^{-1} in the first and second batch, respectively. Due to low concentration of NH_4-N in feedlot wastewater, the depletion of NH_4-N occurred almost within the first week in both batch experiments. This is likely that young plants prefer to utilize NH_4-N to make amino acid and protein (Gupta et al., 2012). The conversion of NH_4-N to protein are easier than NO_2-N+NO_3-N to protein because plants needs stored carbohydrate and enzyme called nitrate reductase with the help of light energy to convert NO_2-N+NO_3-N to NH_4-N if plants uses NO_2-N+NO_3-N. But, form the Hoagland solution, the initial NH_4-N was sufficient for plants (28 mgL^{-1} TN levels for water hyacinth (Gupta et al., 2012)) growth and it was started to deplete from second week. In the first batch, the reduction of NH_4-N was significantly lower after first week of experiment for all plants in both diluted and undiluted feedlot runoff (Figs. 4.16, 4.17 & 4.18). In the first batch, NH_4-N reduction by all three plants grown in Hoagland, runoff (1:1) and runoff (undiluted) were similar (Figs. 4.17 and 4.18). For Hoagland solution, the NH_4-N concentration was significantly reduced by water hyacinth and sorghum than initial concentration after second week of plantation, but it happened in fourth week for water lettuce (Fig. 4.15). In the first batch, the concentration of NH_4-N decreased significantly from the all feedlot runoff and Hoagland solutions within the third week as compared to initial concentration. In the second batch, however, the concentrations of NH_4-N in feedlot runoff were significantly lower than those of initial concentration over the experiment period by all three types of plant (Fig. 4.20). Similarly, in the Hoagland solution, the concentration of NH_4-N reduced significantly by water hyacinth and sorghum after second week of experiment, but it was true for water lettuce after fourth week (Fig. 4.19).

In the first batch, NH_4-N concentration reduction by sorghum was not significantly difference than water hyacinth, but it was significantly higher than water lettuce grown in the Hoagland solution (Fig. 4.15). Though all three types of plants were capable to reduce NH_4-N efficiently from the feedlot runoff towards the end as compared to initial concentration, there were no significant differences in reduction after week 1 (Fig. 4.16). The reduction of NH_4-N concentration was similar in runoff (1:1) and runoff (1:2) for sorghum, but water lettuce reduced significantly higher NH_4-N concentration than water hyacinth (Figs. 4.17 & 7.18). In second batch, water hyacinth and sorghum reduced NH_4-N from the Hoagland solution significantly greater than water lettuce (Fig. 4.19) and almost same for all plants in the feedlot runoff (Fig. 4.20).

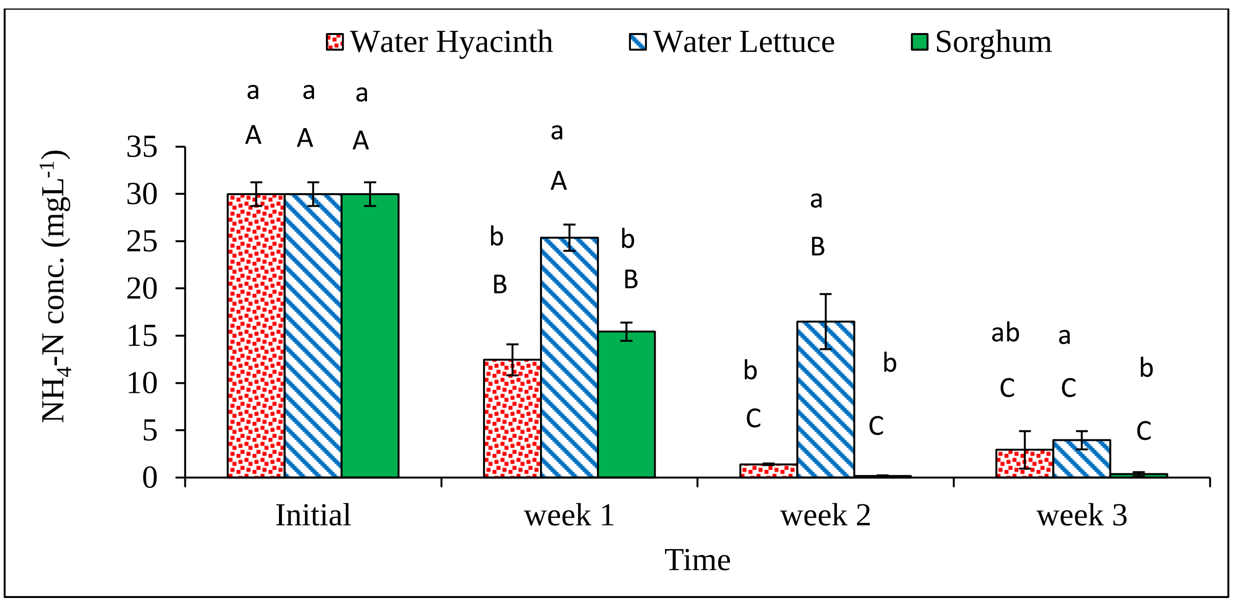

Figure 4.15. Ammonium nitrogen in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

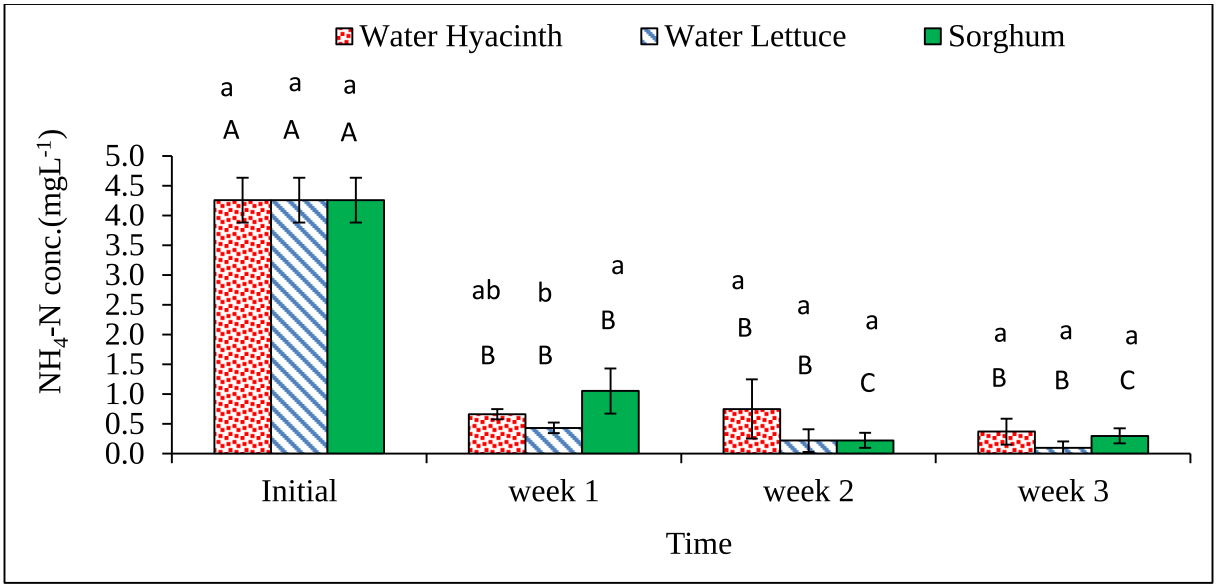

Figure 4.16. Ammonium nitrogen concentration in the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

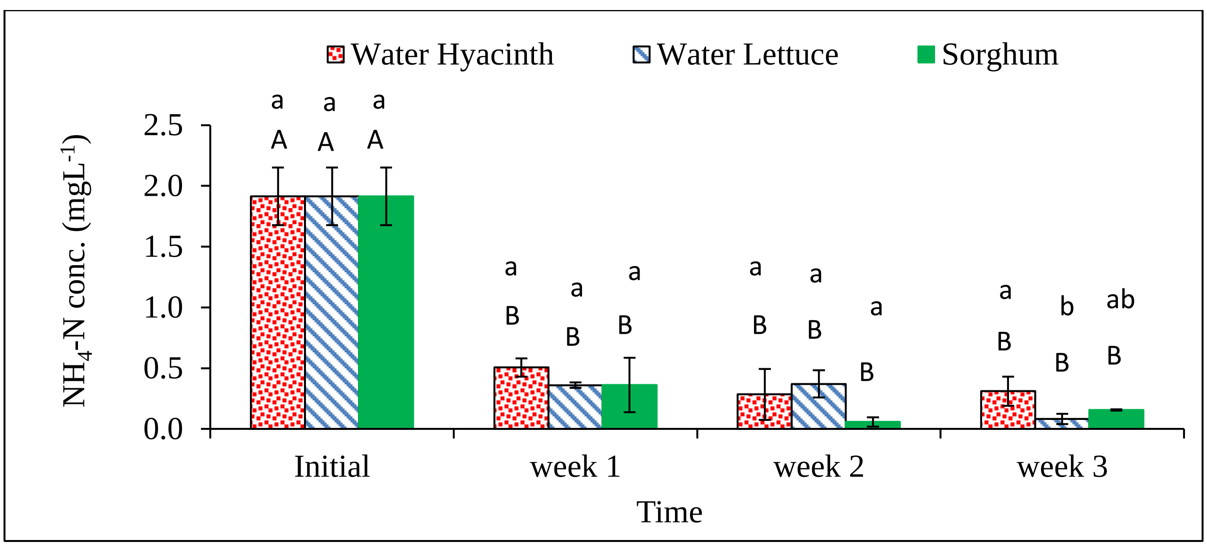

Figure 4.17. Ammonium nitrogen concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

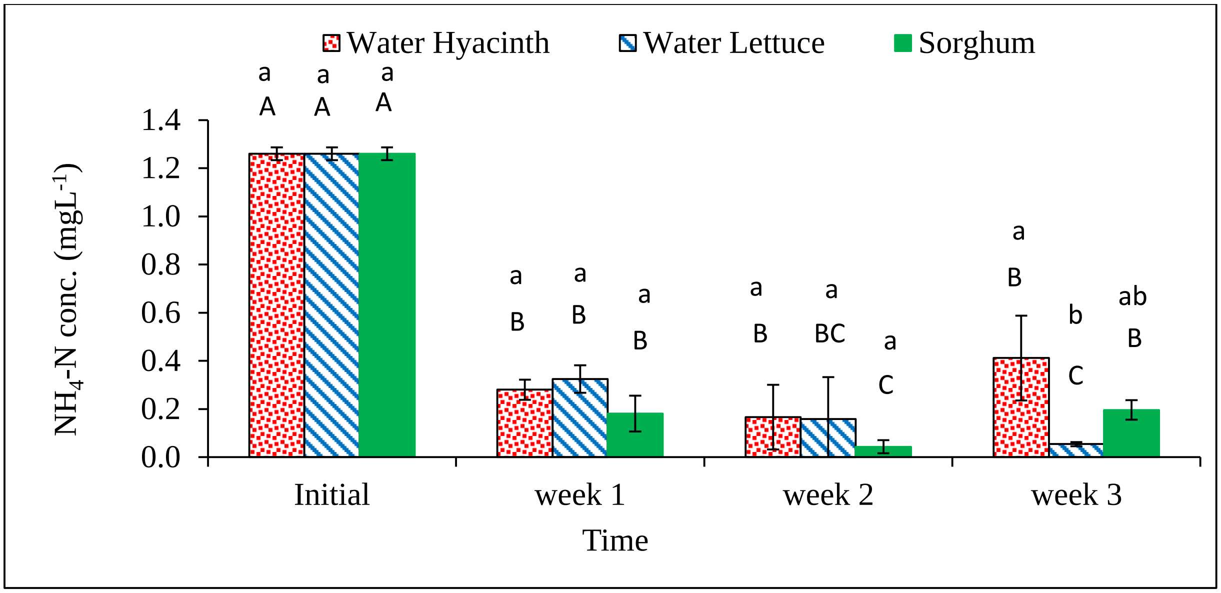

Figure 4.18. Ammonium nitrogen concentration in the runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

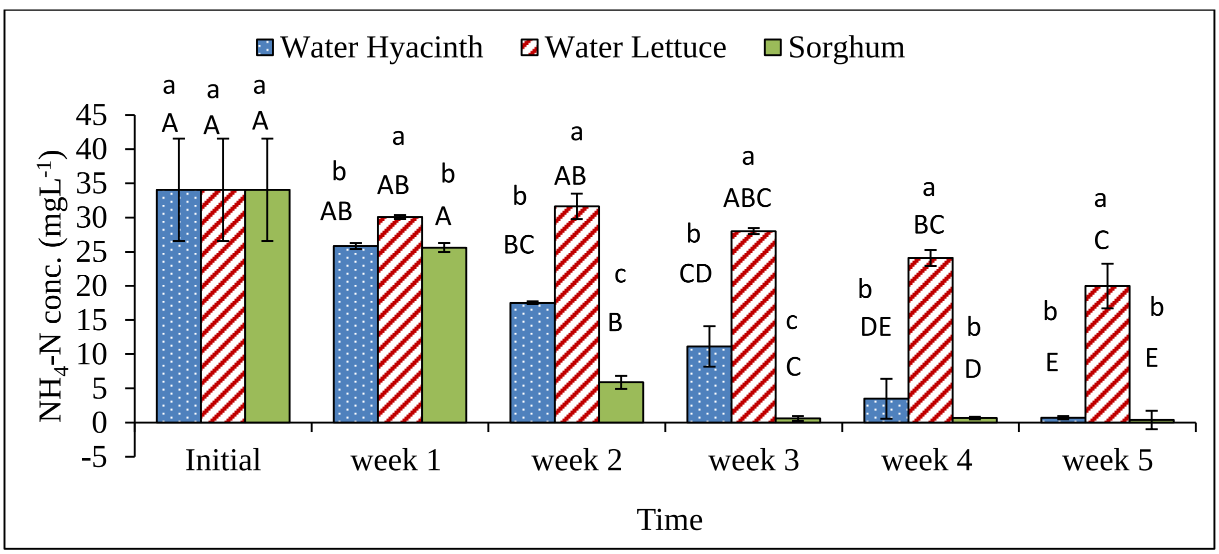

Figure 4.19. Ammonium nitrogen concentration in the Hoagland solution in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

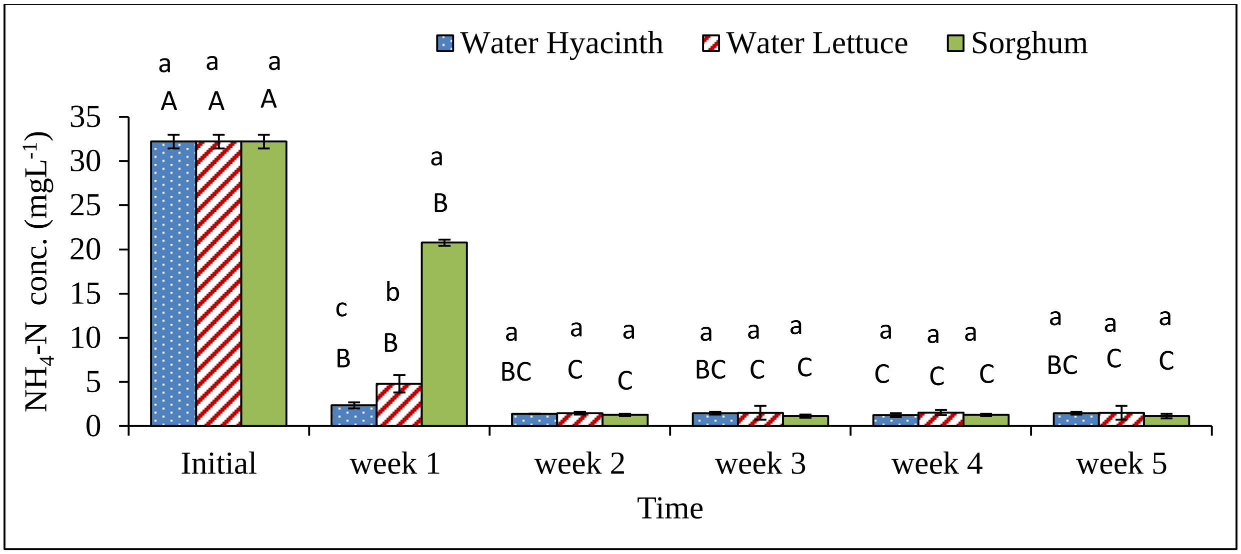

Figure 4.20. Ammonium nitrogen concentration in the runoff (undiluted) in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

4.7. Nitrite and nitrate Nitrogen reduction

Initial concentration of NO_2-N+NO_3-N in feedlot runoff was 1.43 and 0.03 mgL^{-1} in first and second batch, respectively. Similarly, the NO_2-N+NO_3-N in the Hoagland solution was 117.64 mgL^{-1} and 123.5 mgL^{-1} in the first and second batch, respectively. NO_2-N+NO_3-N concentration of feedlot runoff was almost negligible and its contribution to plant growth was also negligible as compared to NO_2-N+NO_3-N concentration in the Hoagland solution. The NO_2-N+NO_3-N are readily absorbed by root tissues and provide nitrogen requirement for the plants growth. As compared to NH_4-N concentration, the NO_2-N+NO_3-N concentration in the Hoagland solution was approximately 4 times greater. Therefore, Hoagland solution provided most of the nitrogen demand of plants throughout the experimental periods. However, for better plant's growth, the sufficient concentration of NO_2-N+NO_3-N is necessary along with NH_4-N. If the Hoagland solution is considered as the controlled solution, then it can be inferred that lower net plant biomass (Figs. 4.1 & 4.2) in feedlot runoff were also due to the lack of proper concentration of NO_2-N+NO_3-N concentration along with solar intensity.

The NO_2-N+NO_3-N concentration in feedlot runoff fluctuated widely due to the nitrification process caused by microbes in feedlot runoff (Sooknah & Wilkie, 2004). These fluctuations in NO_2-N+NO_3-N concentrations were likely due to the resultant effect of nutrient uptake by the plants and nitrate elevation due to nitrification. In feedlot runoff, NO_2-N+NO_3-N concentrations were low (0-1.9 mg L^{-1}) and found to be barely above detection limit of the measuring instrument. Bacteria under aerobic conditions such as plant roots or open feedlot runoff convert NH_4-N to NO_2-N+NO_3-N. The naturally occurring alkaline nature of feedlot runoff (pH= 7.0-8.5) and supplying dissolve oxygen through continuous aeration enhances this nitrification process. The decreased in NH_4-N concentration and increased in NO_2-N+NO_3-N concentration simultaneously in the feedlot runoff water also supports the nitrification process of feedlot runoff samples (Figs 4.16 & 4.22, 4.17 & 23, 4.18 & 4.24, and 4.20 & 4.26). From the first batch, NO_2-N+NO_3-N concentration was significantly different in feedlot solution after one week by water lettuce and after one and third weeks by sorghum (Fig. 4.22). However, weekly measured concentrations of NO_2-N+NO_3-N were not significantly different by water hyacinth in runoff (undiluted) over the experimental period (Fig. 4.22).

Similarly, in runoff (1:1) and runoff (1:2), plant types did not show significant differences in NO_2-N+NO_3-N contributions throughout the experiment except sorghum reduced significant amount of NO_2-N+NO_3-N in the third week (Figs. 4.23 & 4.24). In the Hoagland solution, the concentration of NO_2-N+NO_3-N was significantly different after first week of plantation by sorghum and water lettuce; and after second week by sorghum and water hyacinth. It was found that in week 2 and onward, sorghum reduced NO_2-N+NO_3-N significantly higher compared to initial concentration (Fig. 4.21). In the second batch, there were no significant differences in NO_2-N+NO_3-N concentrations contributed by plants grown in feedlot runoff (Fig. 4.26). Similarly, for the Hoagland solution, all plants reduced NO_2-N+NO_3-N concentrations significantly; however, there were no significantly difference in NO_2-N+NO_3-N concentrations reduced by water hyacinth from first week to third week. Sorghum reduced NO_2-N+NO_3-N concentrations remarkably from week 4 to onward compare to initial concentration (Fig. 4.25). For water lettuce, NO_2-N+NO_3-N concentrations were fluctuating over the experimental period as shown in Fig. 4.25. The contribution of sorghum in reducing NO_2-N+NO_3-N concentration when grown in Hoagland solution was significantly different and higher than those of the water lettuce and water hyacinth.

In the first batch, the NO_2-N+NO_3-N concentration reduction by sorghum was significantly higher than water lettuce and water hyacinth from the Hoagland solution (Fig 4.21). The NO_2-N+NO_3-N concentration reduction by water lettuce and sorghum was not significantly different from each other but significantly lower than the water hyacinth from the runoff (1:1) and runoff (undiluted) (Figs. 4.22 & 4.23). All the plants reduced NO_2-N+NO_3-N concentration equally and there were no significant difference in NO_2-N+NO_3-N reduction from the runoff (1:2) at the end of experiment (Fig 4.24). In second batch experiment, sorghum and water lettuce reduced NO_2-N+NO_3-N concentration the most and the least form the Hoagland solution, respectively, (Fig. 4.25) though it was same for all other plants grown in feedlot runoff (Fig. 4.26).

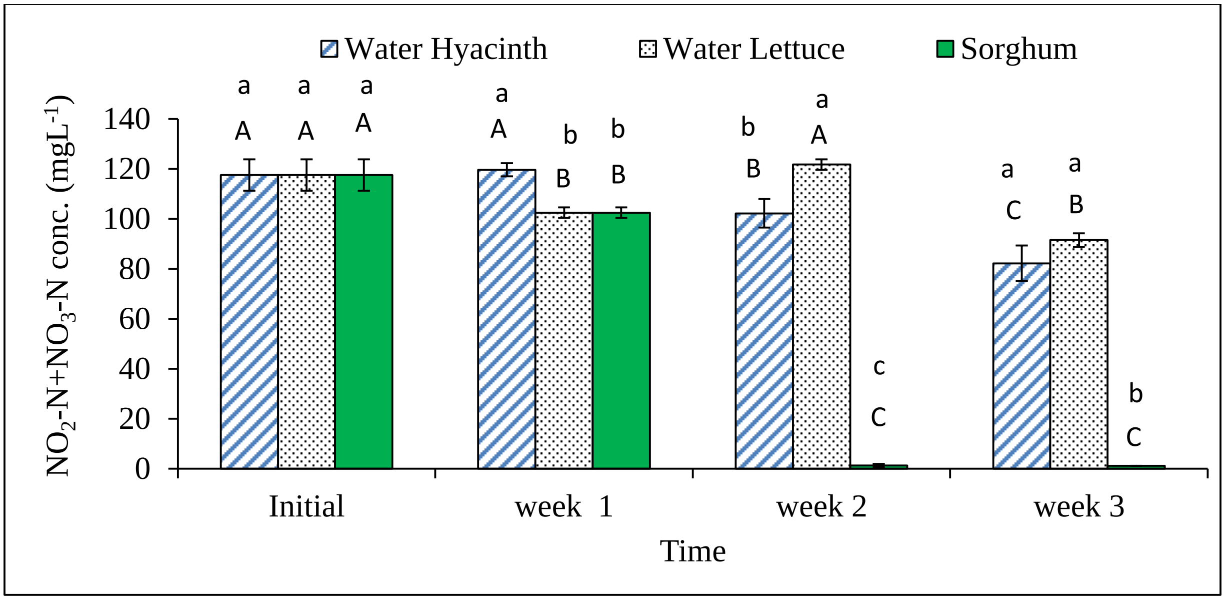

Figure 4.21. Nitrite and nitrate nitrogen concentration in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

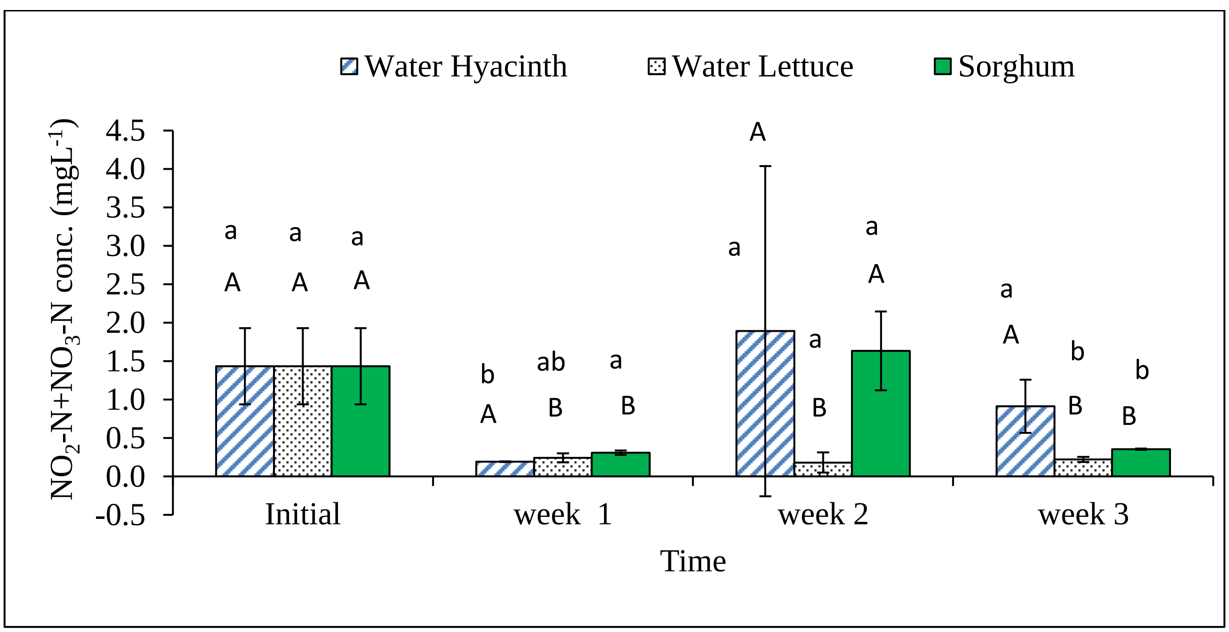

Figure 4.22. Nitrite and nitrate nitrogen concentration in the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

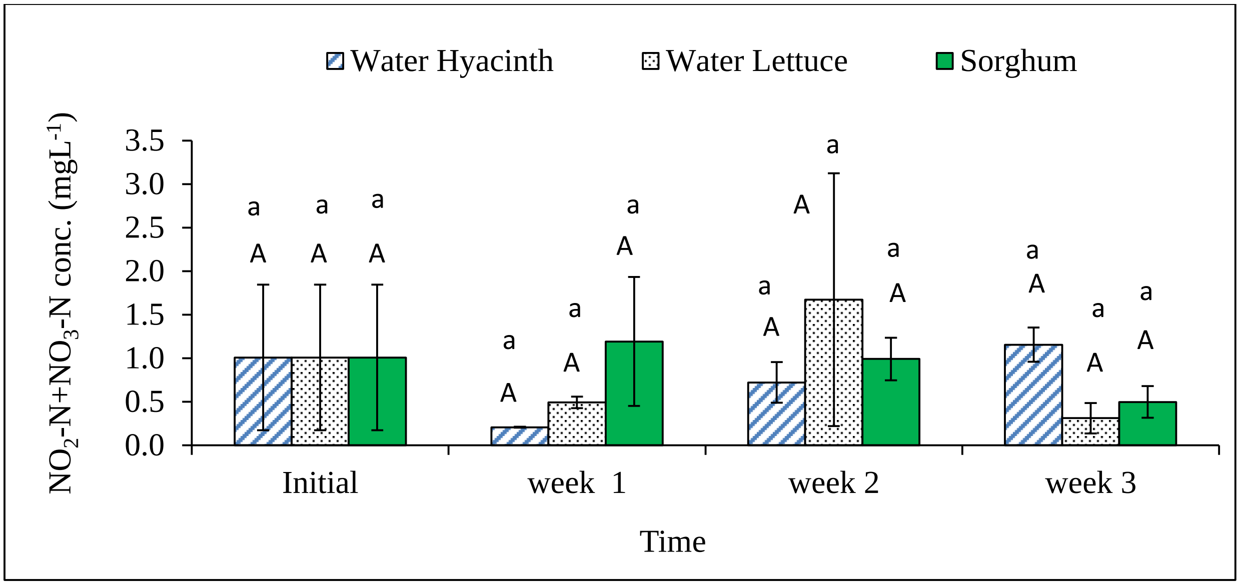

Figure 4.23. Nitrite and nitrate nitrogen concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

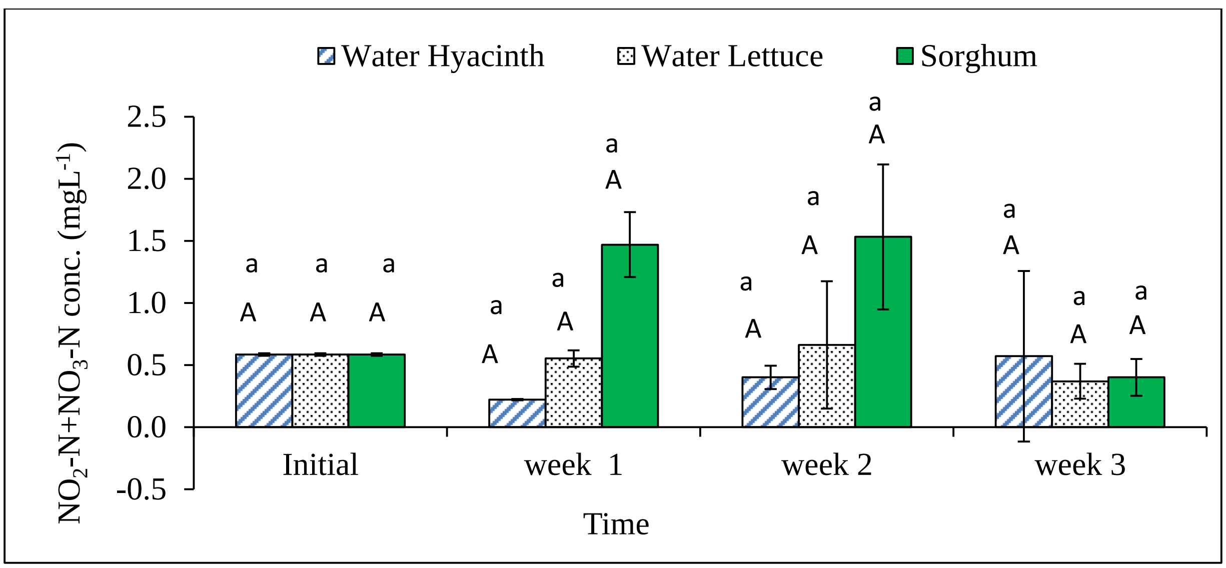

Figure 4.24. Nitrite and nitrate nitrogen concentration in the runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

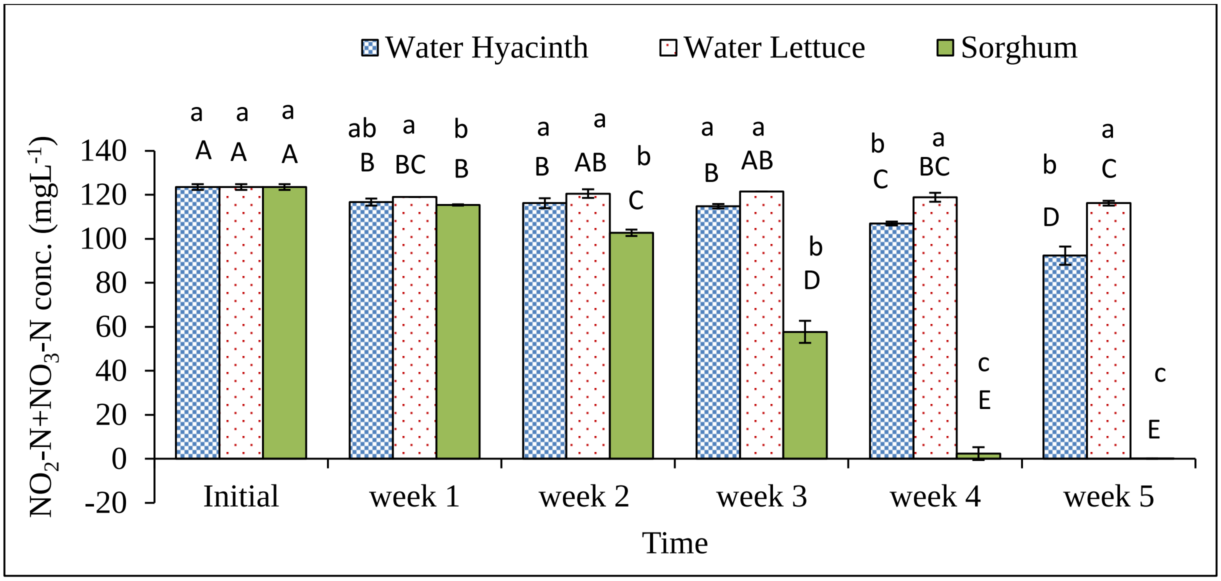

Figure 4.25. Nitrite and nitrate nitrogen concentration in the Hoagland solution in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

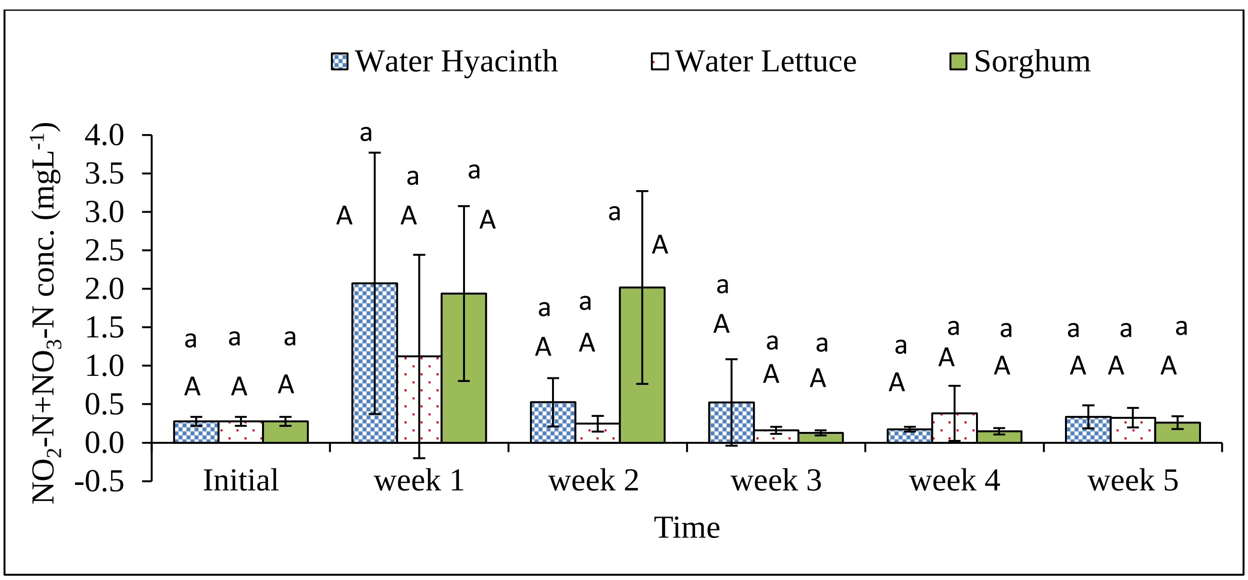

Figure 4.26. Nitrite and nitrate nitrogen concentration in the runoff (undiluted) in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

4.8. Total Kjeldahl Nitrogen reduction

Total Kjeldahl Nitrogen (TKN) is the sum of NH_4-N, and organically bounded nitrogen. Initial TKN concentration of feedlot runoff samples was 53.5 and 217.2 mgL^{-1} in the first and second batch, respectively. Similarly, TKN values in first and second batch Hoagland solution was 64.93 and 99.87 mgL^{-1}, respectively. The TKN concentration in the feedlot runoff in second batch was higher due to the present of a greater amount of organic nitrogen (although it was not measured) because of higher TS value and at the same time it had lower NO_2-N+NO_3-N in feedlot runoff (Tables 4.1 & 4.2). The higher TKN value means there is always chance of ammonification which helps to increase the formation of NH_4-N in water sample (Wall et al., 2013) and requires higher amount of BOD (Scott, 2012). In general, the TKN present in the wastewater samples are mainly reduced by plant uptake in the form of NH_4-N, NH_3 volatilization, nitrification, and entrapment of particulate matter by the root of plants (Sooknah & Wilkie, 2004). In this experiment, most of the TKN reduction was due to the uptake of plants since occurrence of the ammonification process of TKN was weakly demonstrated (Figs. 4.18 and 4.30). The TKN concentration reduction were much lower than those of NH_4-N and NO_2-N+NO_3-N because plants cannot uptake TKN directly until organic nitrogen is mineralized into NH_4-N via ammonification, volatilization or the nitrification process by microorganism, heat, oxygen etc.

The results from both of these experiments show that TKN concentrations of each plant at each sampling event (week) were significantly lower in comparison to initial (starting day 1) concentrations and showed decreasing trends over the experimental period when used runoff (undiluted; Fig. 4.28). Similar patterns of TKN concentrations were also observed for runoff (1:1) and runoff (1:2) (Figs. 4.29 and 4.30), but significantly lower concentration of TKN was observed after two weeks of plantation as compared to initial concentration. In the Hoagland solution, sorghum and water hyacinth reduced significant concentration of TKN after first week but water lettuce reduced significant amount of TKN after second weeks (Fig. 4.27). In the second batch with feedlot runoff (undiluted), sorghum outperformed water lettuce and water hyacinth in reducing TKN concentration and showed a decreasing trend over the experiment period starting from week 1 (Fig. 4.32). Water hyacinth and water lettuce reduced significant amount of TKN after third and fourth weeks, respectively (Fig. 4.32). In the Hoagland solution, water hyacinth reduced TKN concentration significantly after first week followed by sorghum and water lettuce as the experiment progressed (Fig. 4.31).

In comparision to sorghum and water lettuce, water hyacinth significantly reduced TKN from the Hoagland solution (Fig. 4.27) though it was not significantly different from the runoff (1:1), runoff (1:2), and runoff (undiluted) at the end of first batch experiment (Figs. 4.28 to 4.30). In the second batch, all plants reduced TKN concentration significantly, but water hyacinth reduced TKN concentration the most and water lettuce reduced the least amount of TKN from the Hoagland solution (Fig. 4.31). The TKN reduction from the feedlot runoff was not significantly different for all plants at the end of second batch (Fig. 4.32). The reduction of TKN was not significantly different for water hyacinth, water lettuce and sorghum in the feedlot runoff (undiluted) that could be due to the presence of organically bounded nitrogen or lower rate of ammonification process.

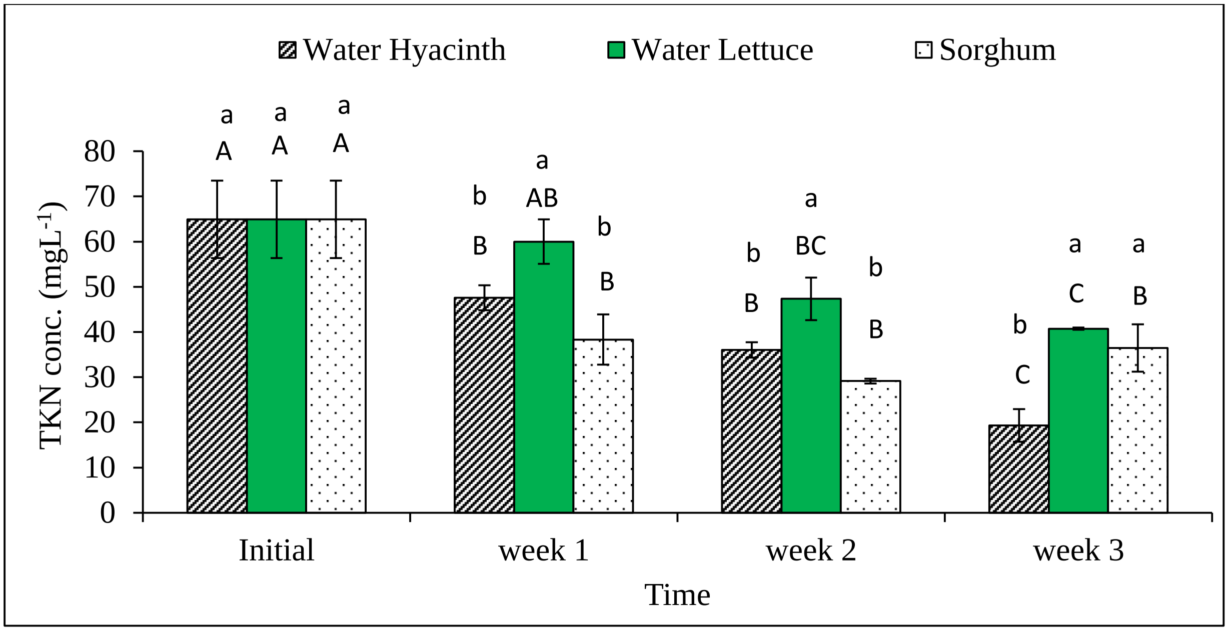

Figure 4.27. Total Kjeldahl Nitrogen concentration in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

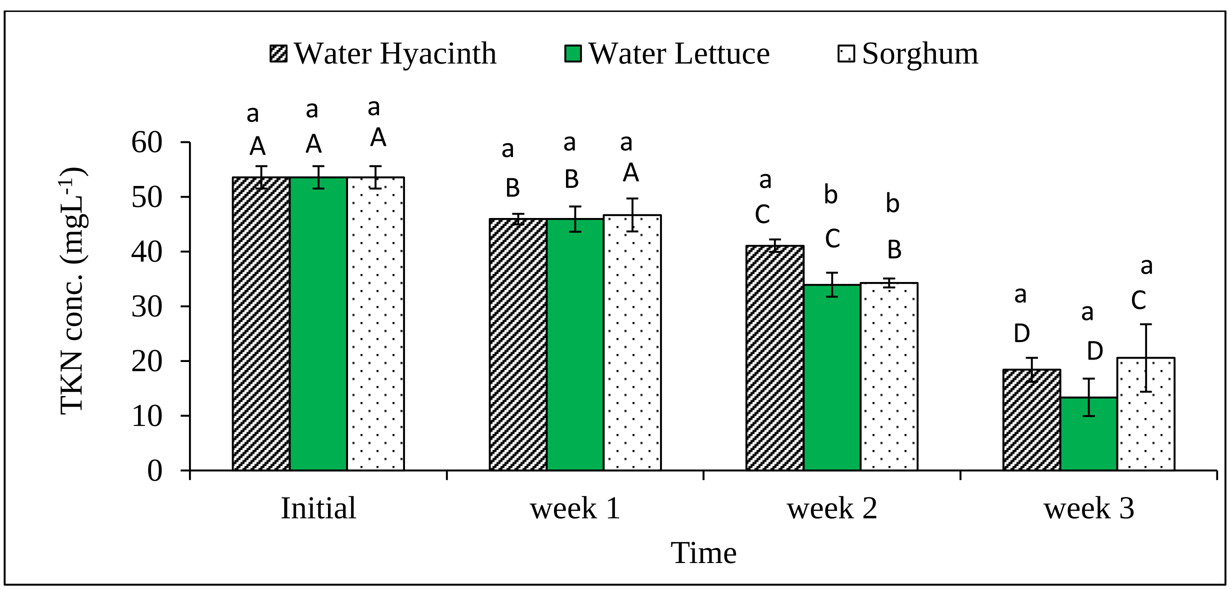

Figure 4.28. Total Kjeldahl Nitrogen concentration the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

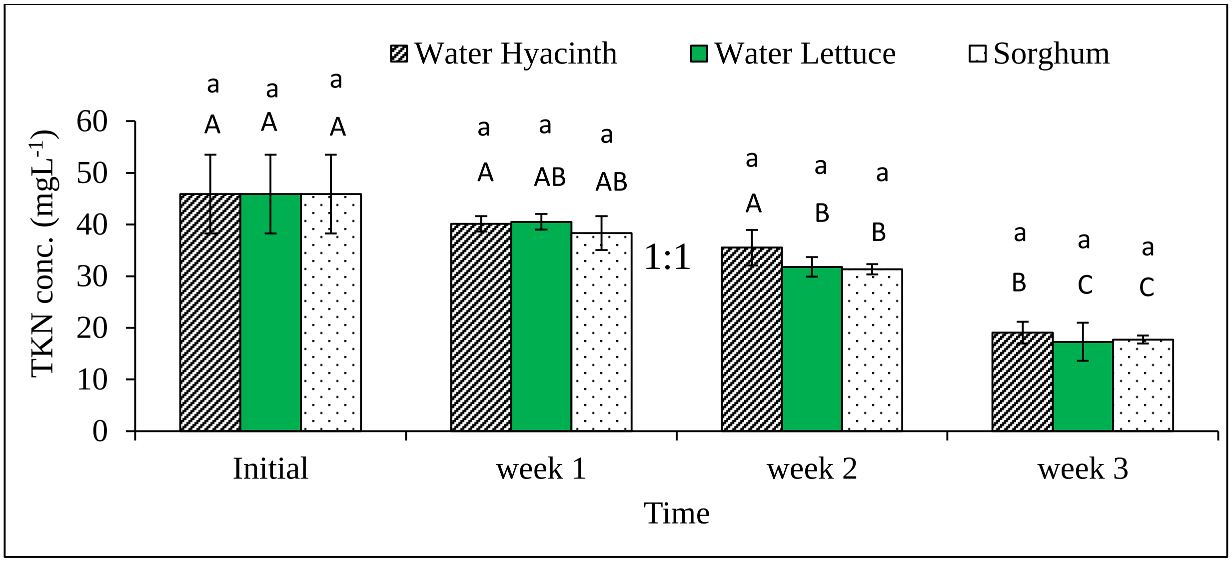

Figure 4.29. Total Kjeldahl Nitrogen concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

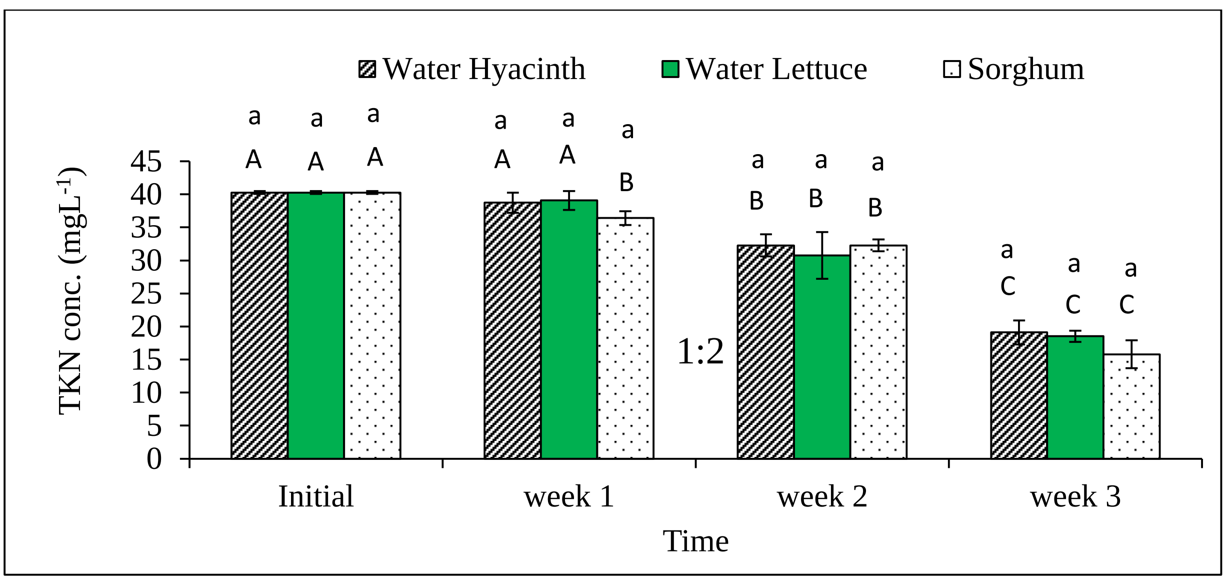

Figure 4.30. Total Kjeldahl Nitrogen concentration in the runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

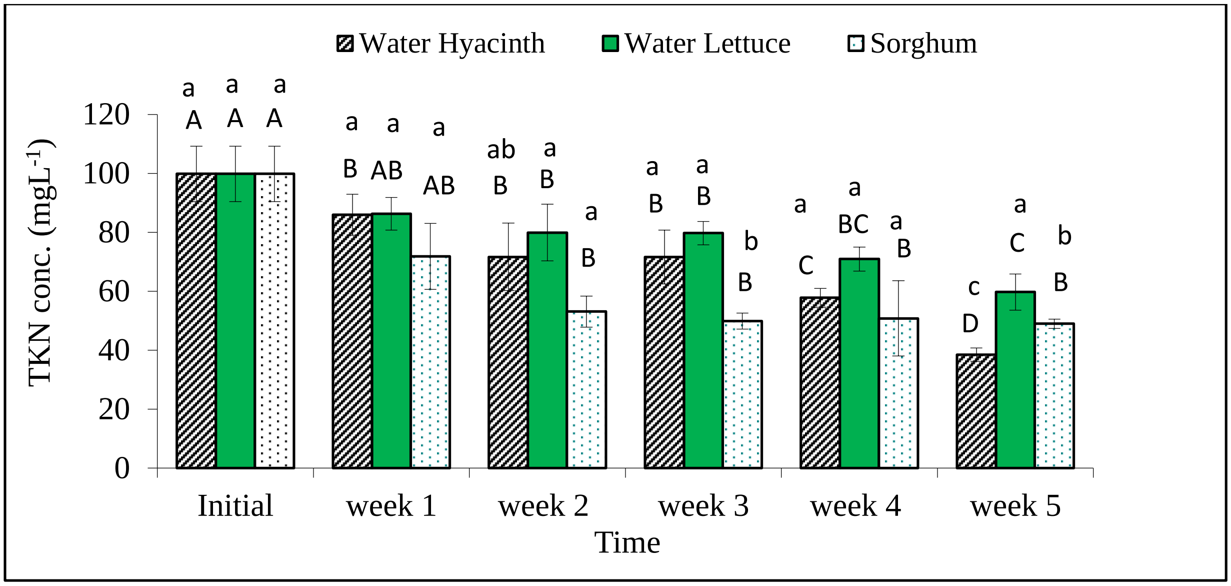

Figure 4.31. Total Kjeldahl Nitrogen concentration in the Hoagland solution in the second experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

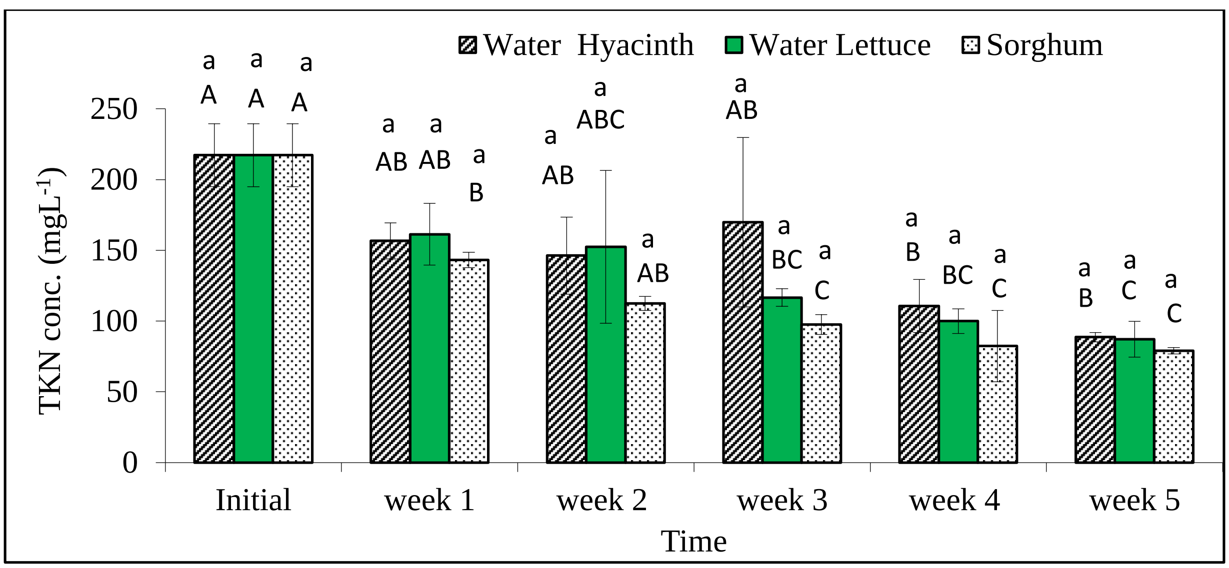

Figure 4.32. Total Kjeldahl Nitrogen concentration in the runoff (undiluted) in the second experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

4.9. Potassium reduction

The requirement of K for the plants ranged from 10 to 83 mgL^{-1} depending on the plant species (Gupta et al., 2012). In the first batch, the K concentration of feedlot runoff (57.23 mgL^{-1}) was approximately half of Hoagland solution (144.77 mgL^{-1}). In contrast, the potassium concentration of the feedlot runoff (777.7 mgL^{-1}) was 5.5 times higher than that of the Hoagland solution (134.67 mgL^{-1}) in the second batch. This wide variation in K concentration of feedlot runoff was due to different in feedlot runoff sample collection locations (runoff retention pond and immediate downstream of feedlot). Although there was wide variability in K concentrations, but it was not a limiting factor to grow plants used in this experiment.

The K was well up taken by water hyacinth and sorghum plants from feedlot runoff (undiluted) during the first batch. In the first batch, water hyacinth and sorghum in feedlot runoff reduced significant amount of K concentration after first week of plantation and water lettuce reduced K significantly after second week (Fig. 4.34). In runoff (1:1), water hyacinth reduced K concentration after the first week, but water lettuce and sorghum reduced K concentration significantly after second week (Fig. 4.35). In runoff (1:2), there were no significant differences in K uptake over experiment period by all plants (Fig. 4.36). In the Hoagland solution, the K uptake was significantly different for sorghum after second week of plantation and for other two plants was after third week (Fig. 4.33). In the second batch with feedlot runoff (undiluted), the reduction of K concentration by sorghum was more than other two plants during experiment periods. The reduction of K concentration was significantly different for water lettuce from the first week of plantation. For water hyacinth and sorghum, the K concentration was significantly different from the second weeks of plantation (Fig. 4.38). In the Hoagland solution, sorghum plants uptake significantly more K than water lettuce and water hyacinth from week 1 onward.

The water lettuce showed least amount of K uptake and its concentration measured at fifth week was only significantly different from initial value (Fig. 4.37).

In the first batch, sorghum reduced significantly higher K concentration than water hyacinth and water lettuce from the Hoagland solution (Fig. 4.33). Similarly, water hyacinth and sorghum reduced significantly higher K concentration than the water lettuce in first batch (Figs. 4.34, 4.35 & 4.36) when plants were grown in runoff (1:1), runoff (1:2) and runoff (undiluted). In the second batch, though the reduction of K concentration was not significantly different for all plants from the feedlot runoff (Fig. 4.38), it was significantly different among plant types from the Hoagland solution. Sorghum reduced significantly higher K concentration and water lettuce reduced significantly least concentration of K (Fig. 4.37).

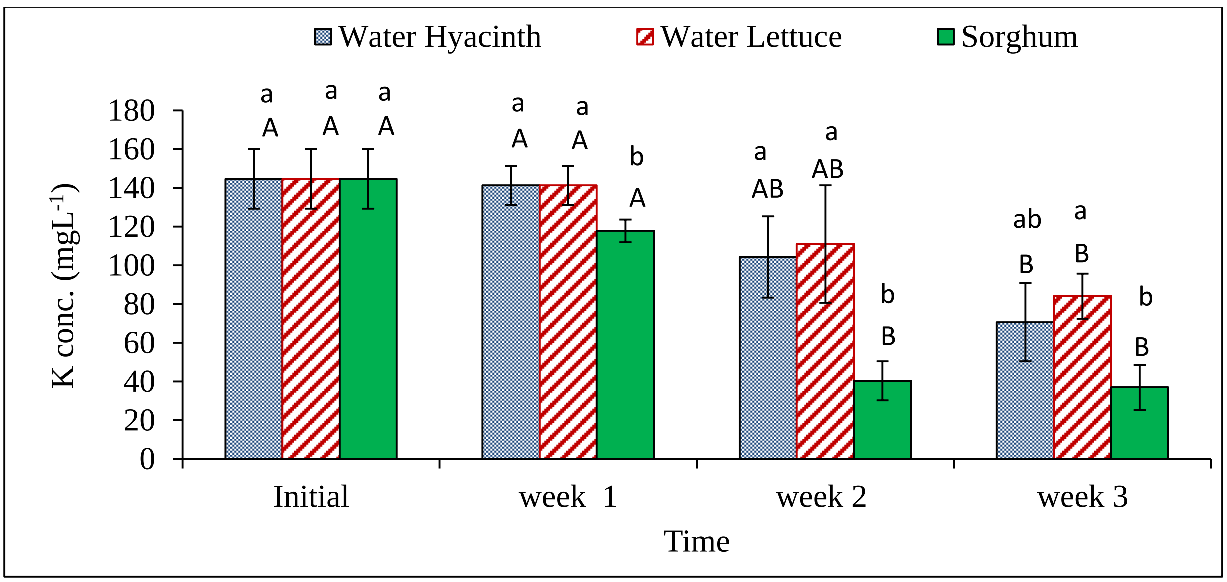

Figure 4.33. Potassium concentration in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

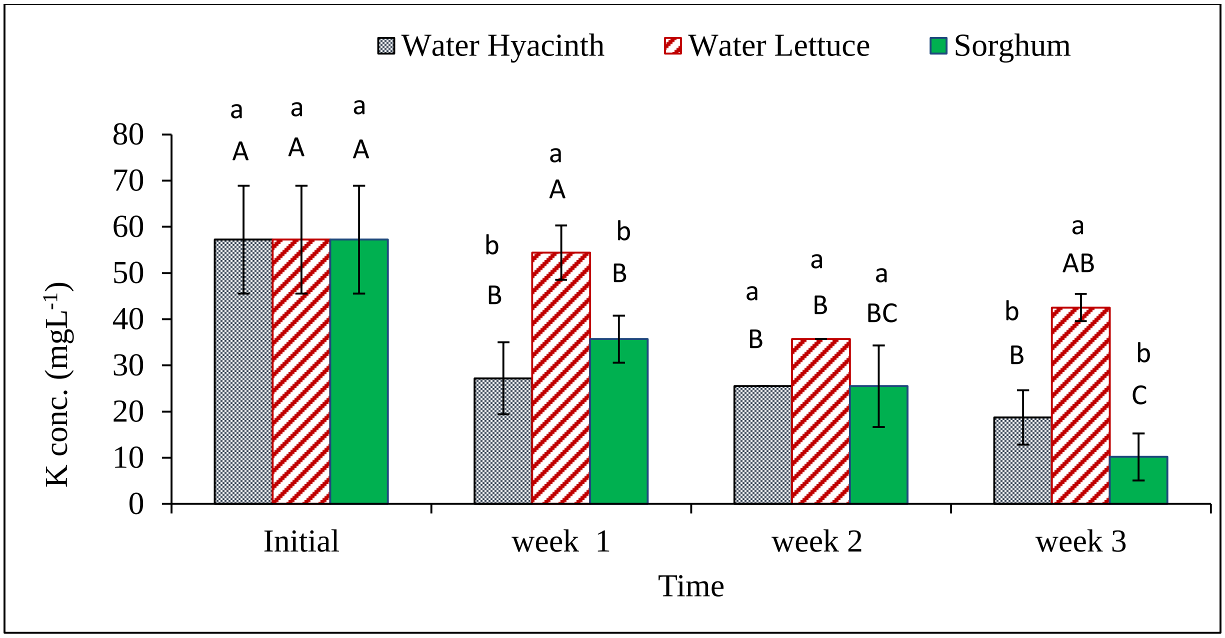

Figure 4.34. Potassium concentration in the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

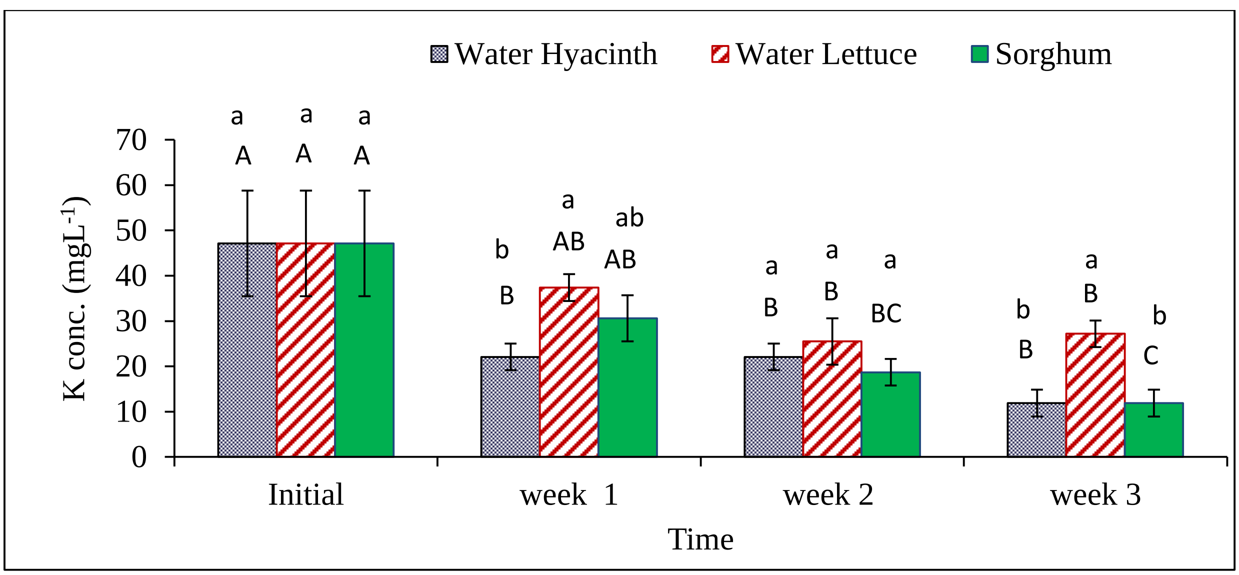

Figure 4.35. Potassium concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

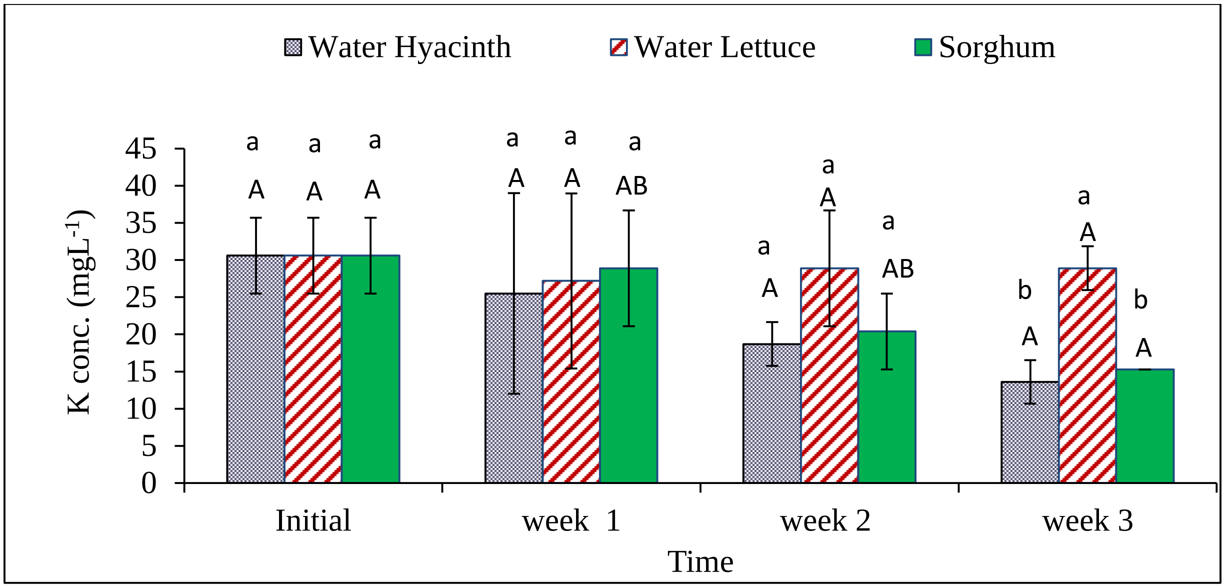

Figure 4.36. Potassium concentration in the runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

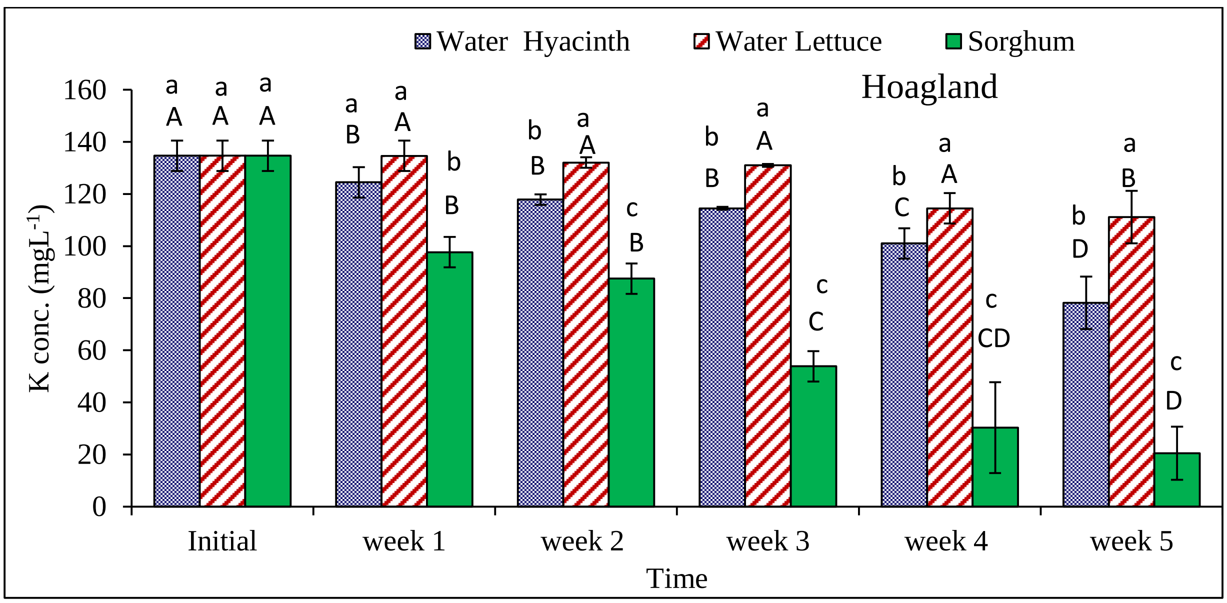

Figure 4.37. Potassium concentration in the Hoagland solution in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

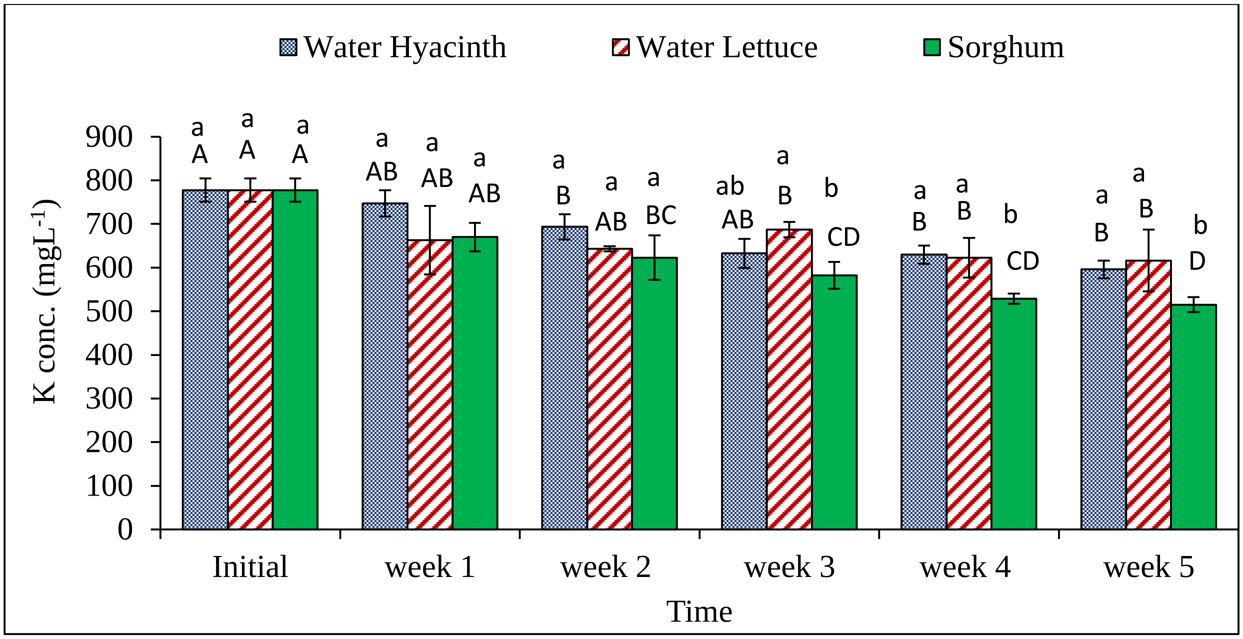

Figure 4.38. Potassium concentration in the runoff (undiluted) in second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

4.10. Ortho-Phosphorus reduction

Among different types of phosphate, OP is readily available for plants. Therefore, its concentration plays a vital role for plant growth. From the analysis of feedlot runoff, orthophosphate were 8.23 and 13.69 mgL^{-1} in feedlot runoff and 66.47 and 64.83 mgL^{-1} in the Hoagland solution in first and second batch experiment, respectively. Feedlot runoff samples had about 8 times and 4 times lower OP concentration than the Hoagland solution during the first and second, respectively. The measured OP during the first batch feedlot of runoff almost depleted within two weeks of experiment for all the plants (Figs. 4.40, 41 & 4.42). However, the OP concentration during the second batch of feedlot runoff fluctuated remarkably (Fig. 4.44). The main reason of these OP fluctuations in feedlot runoff experiment might be the release of OP from the TP because the TP concentration in second batch of feedlot runoff was about 6 times greater than the TP concentration present in first batch of feedlot runoff. Additionally, from the plant net biomass and the OP concentration data, it can be concluded that higher OP can contribute greater net plant biomass (Figs. 4.1, 4.2 compare with Figs 4.39 & 4.43). In the first batch, the OP uptake by all three plants from the runoff (1:1) and runoff (undiluted) was significantly different after first week of experiment as compared to initial (Figs. 4.40 & 4.41). Similarly, with feedlot runoff (1:2), the OP uptake by all plants were significantly different after second week of experiment (Fig. 4.42). In the Hoagland solution, sorghum and water lettuce uptake more amount of OP and OP concentration was significantly lower from second week of the experiment. There were significant differences in OP uptake by water hyacinth in Hoagland solution at the third week of the experiment (Fig. 4.39).

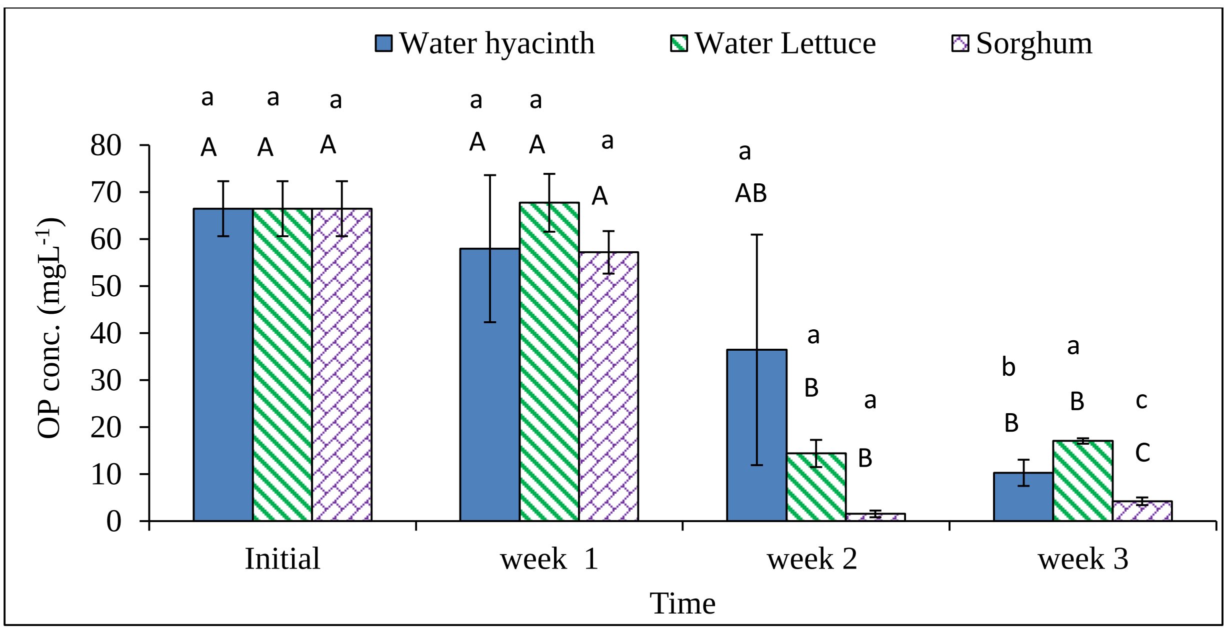

Figure 4.39. Orthophosphate concentration in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

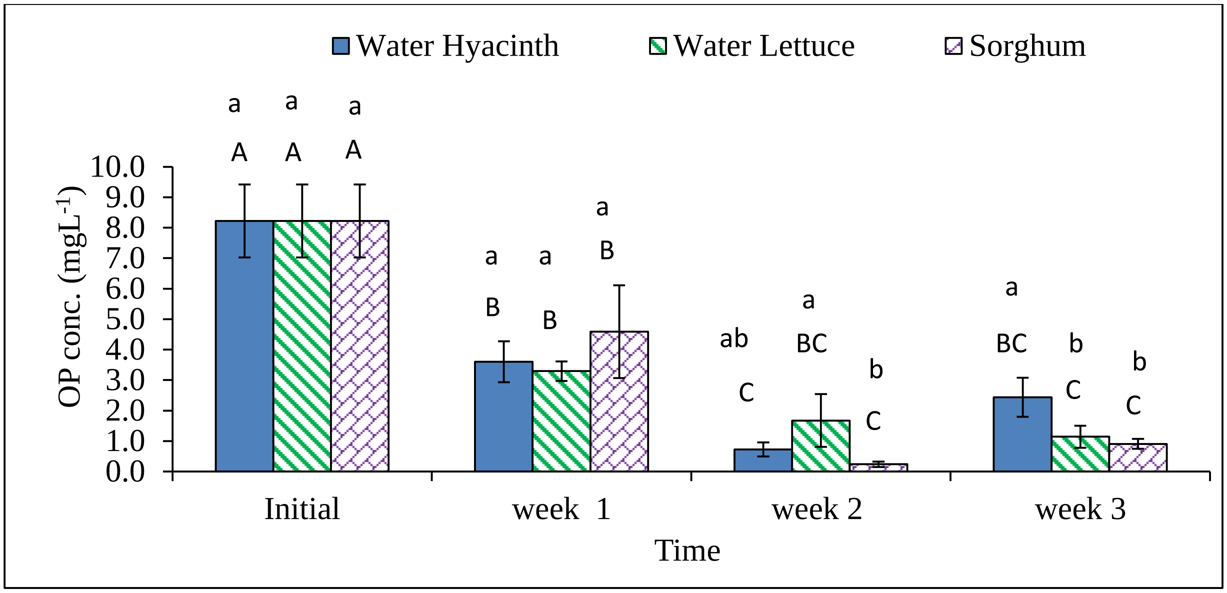

Figure 4.40. Orthophosphate concentration in the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

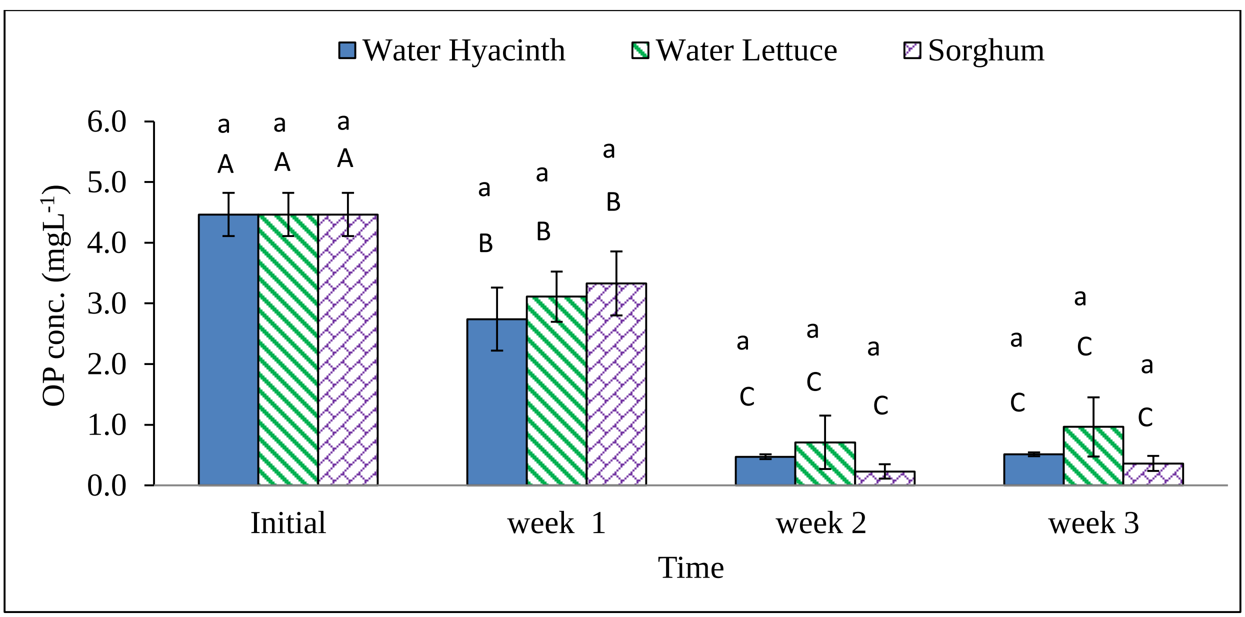

Figure 4.41. Orthophosphate concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

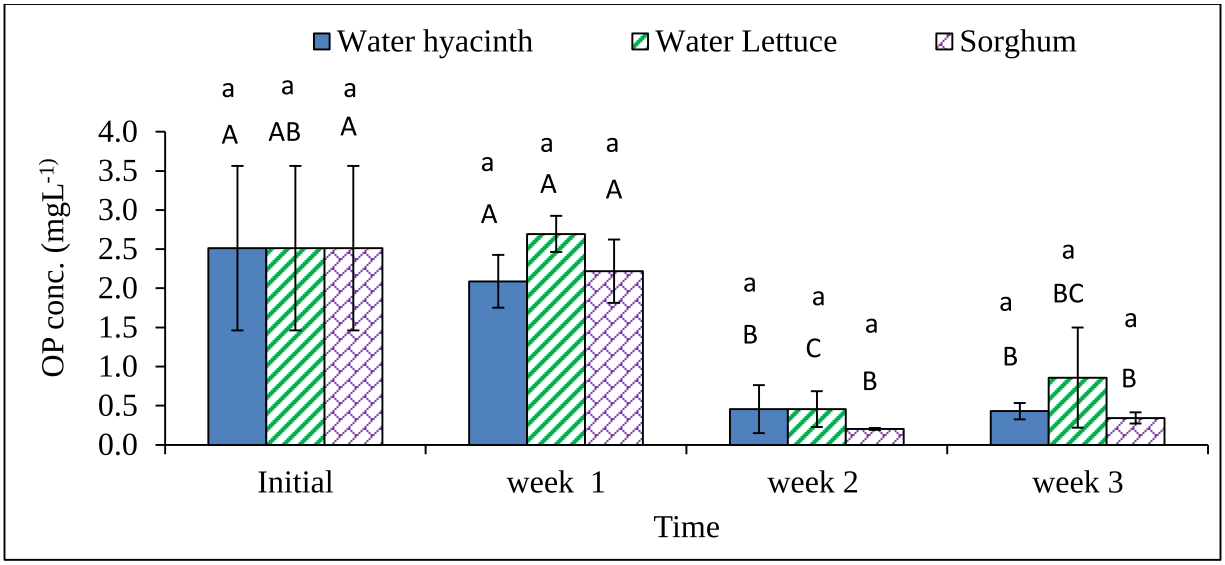

Figure 4.42. Orthophosphate concentration in the runoff (1:2) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

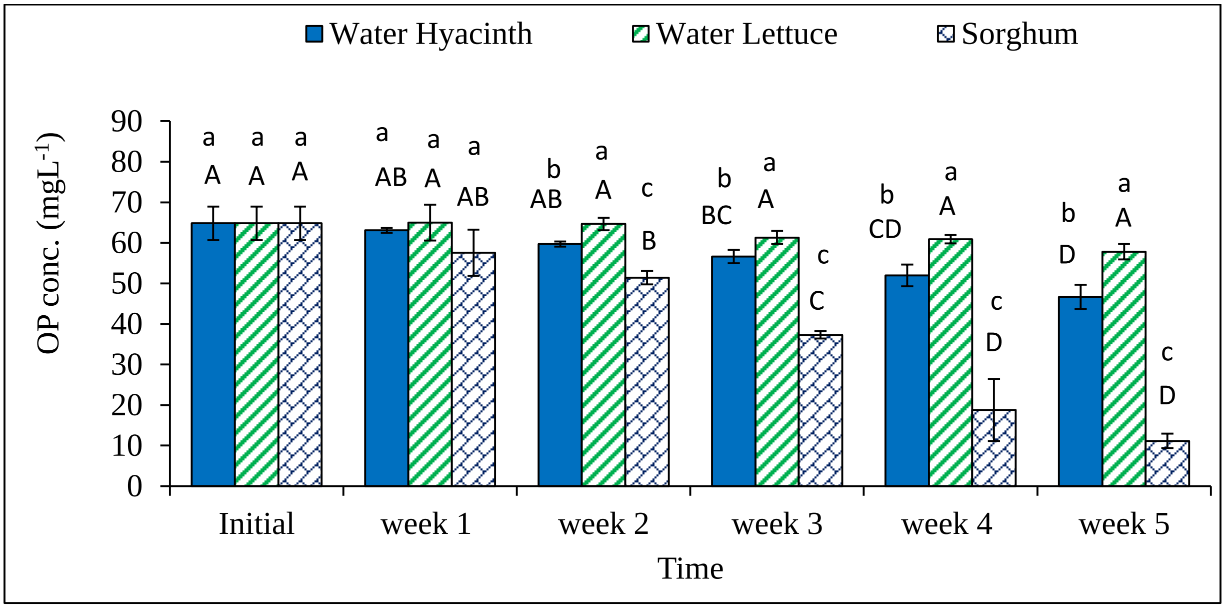

Figure 4.43. Orthophosphate concentration in the Hoagland solution in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at $p \leq 0.05$.

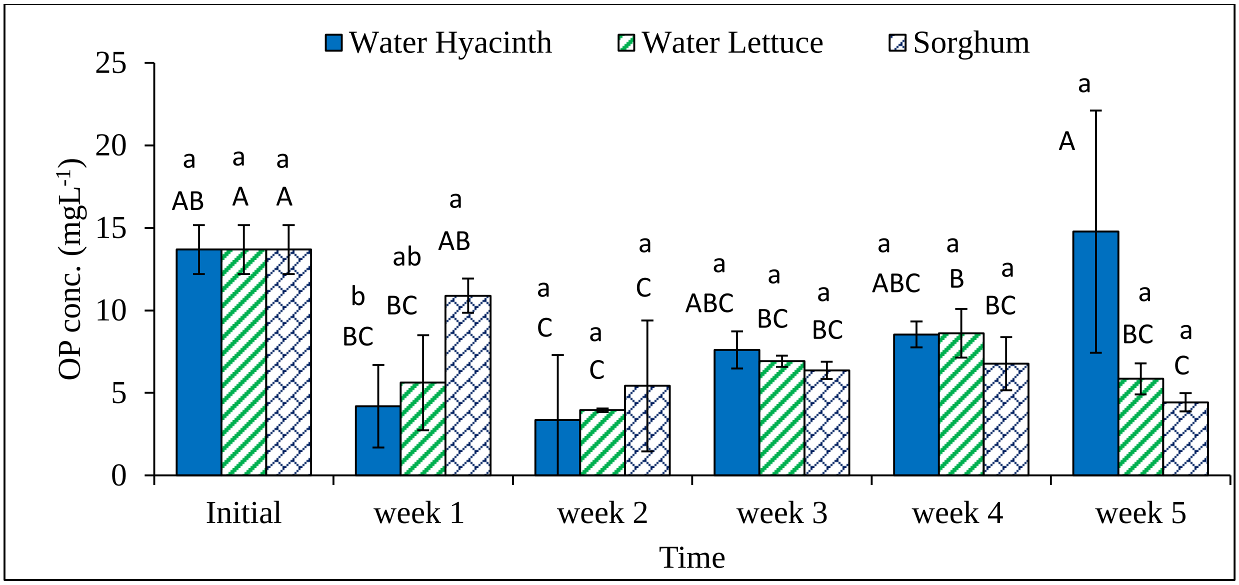

Figure 4.44. Orthophosphate concentration in the runoff (undiluted) in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

In the second batch, wide fluctuations of OP concentration were obtained for all plants in feedlot runoff as shown by error bar in Fig. 4.44. The OP concentration increased in feedlot runoff might be the release of OP from the TP. The feedlot runoff seeded with water lettuce shown significant reduction in OP concentration throughout the experiment periods. However, for water hyacinth seeded sample was significantly lower OP concentration only in first and second weeks and sorghum seeded sample was significantly lower OP concentration after second weeks than the initial OP concentration. In the Hoagland solution, sorghum reduced significant amount of OP since second week. thereafter, water hyacinth reduced significant amount of OP from the third week ownwards. However, the reduction of OP by water lettuce was negligible throughout the experiment period.

At the end of first batch, the OP concentration in the Hoagland solution was significantly different among plants. Sorghum uptake significantly higher OP concentration followed by water hyacinth (Fig. 4.39). For feedlot runoff, water lettuce and sorghum reduced significantly higher OP than water hyacinth (Fig. 4.40) though it was almost same for all plant from the runoff (1:1) and runoff (1:2) (Figs. 4.41 & 4.41). In second batch, plants grown in feedlot runoff did not show any significance difference in OP reduction (Fig. 4.44). In the Hoagland solution, sorghum and water lettuce reduced the highest and the least amount of OP at the end of experiment, respectively (Fig. 4.43).

4.11. Total Phosphorus reduction

TP in feedlot runoff generally contributed to OP concentrations by bacteria, fungus, and other chemical reaction (Arcand & Schneider, 2006). Therefore, TP concentration also plays a vital role for plant growth though it is not readily available to plant as OP. TP concentrations measured during the first and second batch of feedlot runoff were 16.53 and 95.70 mgL^{-1}, respectively, and with the Hoagland solution were 175.92 and 168.17 mgL^{-1}, respectively. In the first batch of feedlot runoff, TP concentration was 10 times less than Hoagland solution but in the second batch, TP concentration was about half of that present in Hoagland solution. Although, TP concentration in runoff samples used for seeding plants were much lower than the Hoagland solution, but it was not a limiting factor to grow plants, but biomass amount might have some effect.

All three plants uptake TP from the feedlot runoff significantly (Fig. 4.46). The uptake of TP from the feedlot runoff during first batch was almost all but less amount than second batch experiment. This was likely due to the lower concentrations of TP and OP (16.5 and 8.2 mg L^{-1}, respectively) present in first batch than second batch (96 and 13.7 mg L^{-1}, respectively). The water hyacinth and sorghum significantly reduced TP concentration from the second weeks of plantation from the runoff (undiluted). Similarly, In the first batch experiment, the concentration of TP in runoff (1:2) and runoff (undiluted) was significantly lower in second week of plantation than the initial concentration for all plants ($p<0.05$; Figs. 4.46 & 4.48). In the runoff (1:1), the concentration of TP was significantly lower from second week of plantation for water hyacinth and sorghum, and third week of plantation for water lettuce (Fig. 4.47). For the Hoagland solution, TP concentration reduced significantly by water hyacinth in second weeks and sorghum in third weeks of experiment. However, water lettuce did not reduce TP concentration significantly thorough out the experiment periods (Fig. 4.45).

Similarly, in the second batch with the Hoagland solution, only sorghum reduced TP concentration significantly after second week onward (Fig 4.49). In the second week, water lettuce and sorghum reduced significant amounts of TP in first week of experiment and water hyacinth reduced significant amount of TP in second-week of plantation from the feedlot runoff as compared to initial (Fig. 4.50).

In first batch, sorghum and water lettuce reduced significantly greatest and lowest amount sof TP from the Hoagland solution, respectively (Fig. 4.45). From feedlot runoff, water lettuce and sorghum reduced significantly higher TP than the water lettuce (Fig. 4.46). The reduction of TP was not significantly different by the plants type from the runoff (1:1) and runoff (1:2) (Figs. 4.46 & 4.47). In second batch, sorghum reduced significantly greatest and water lettuce reduced significantly lowest TP from the Hoagland solution (Fig. 4.49). Similarly, from the feedlot runoff, water hyacinth and sorghum reduced significant concentration of TP than the water lettuce (Fig. 4.50).

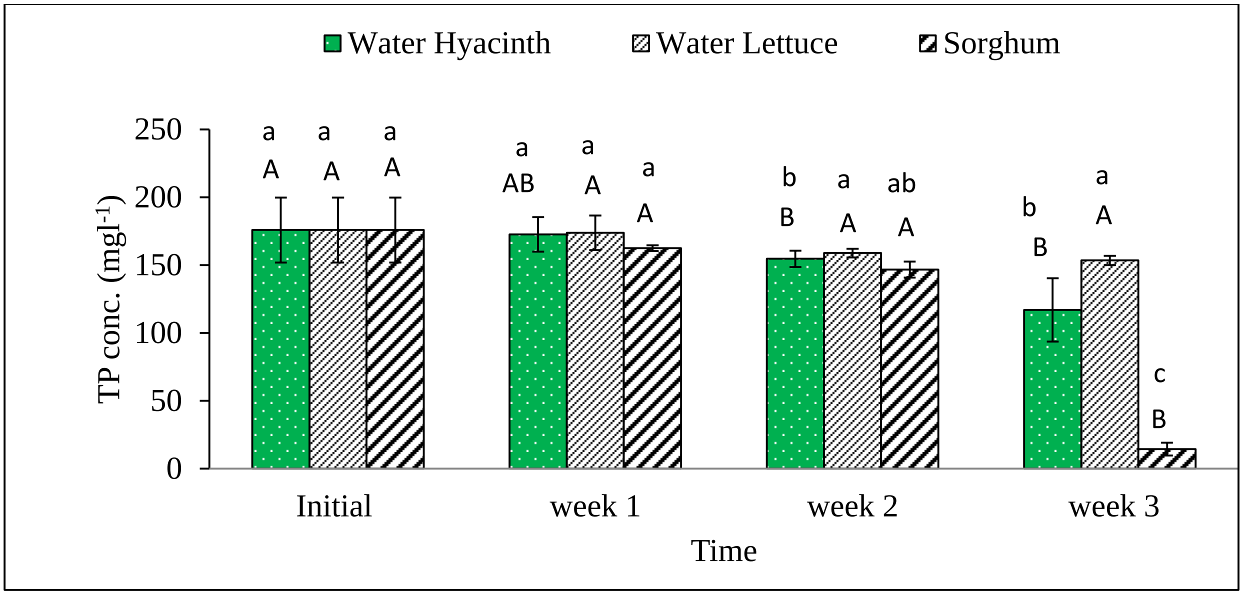

Figure 4.45. Total phosphorus concentration in the Hoagland solution in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

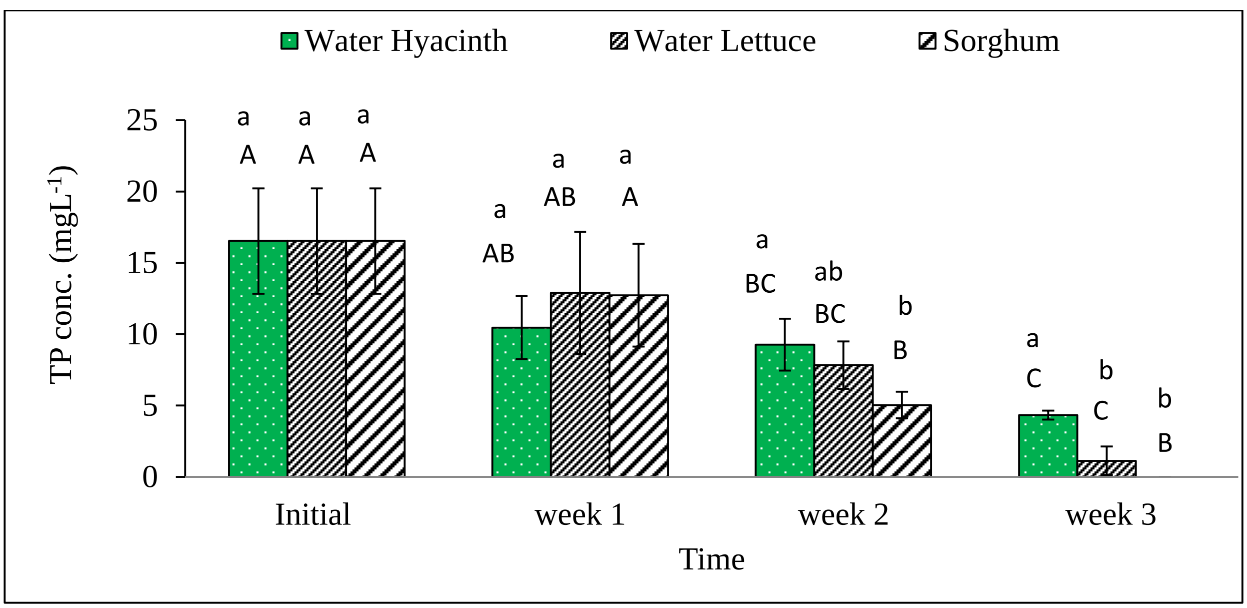

Figure 4.46. Total phosphorus concentration in the runoff (undiluted) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

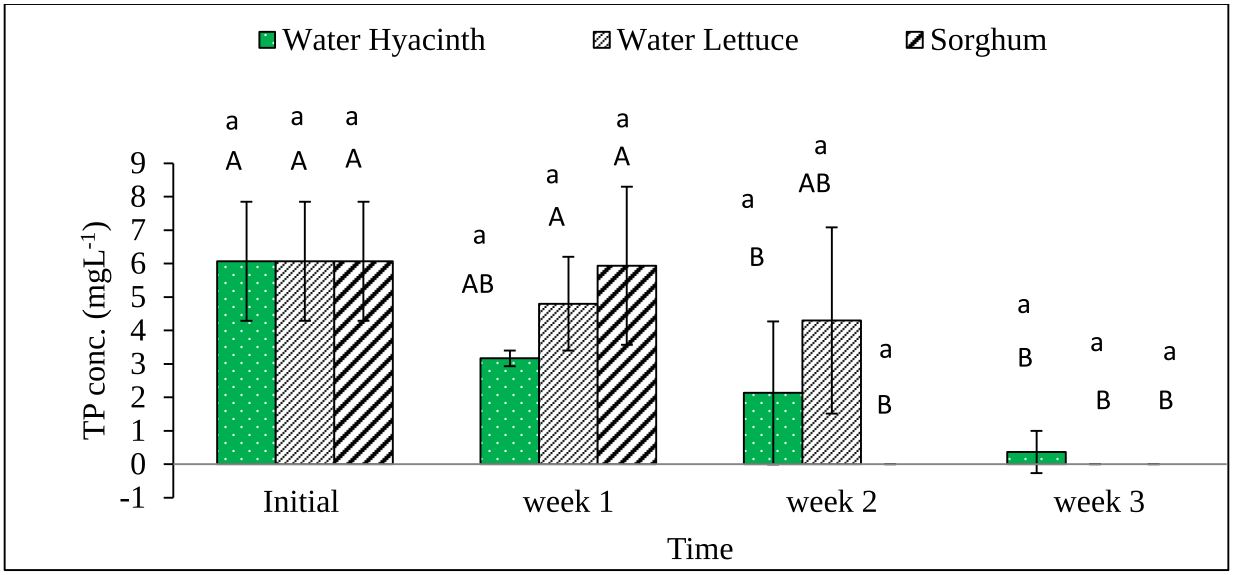

Figure 4.47. Total phosphorus concentration in the runoff (1:1) in the first batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

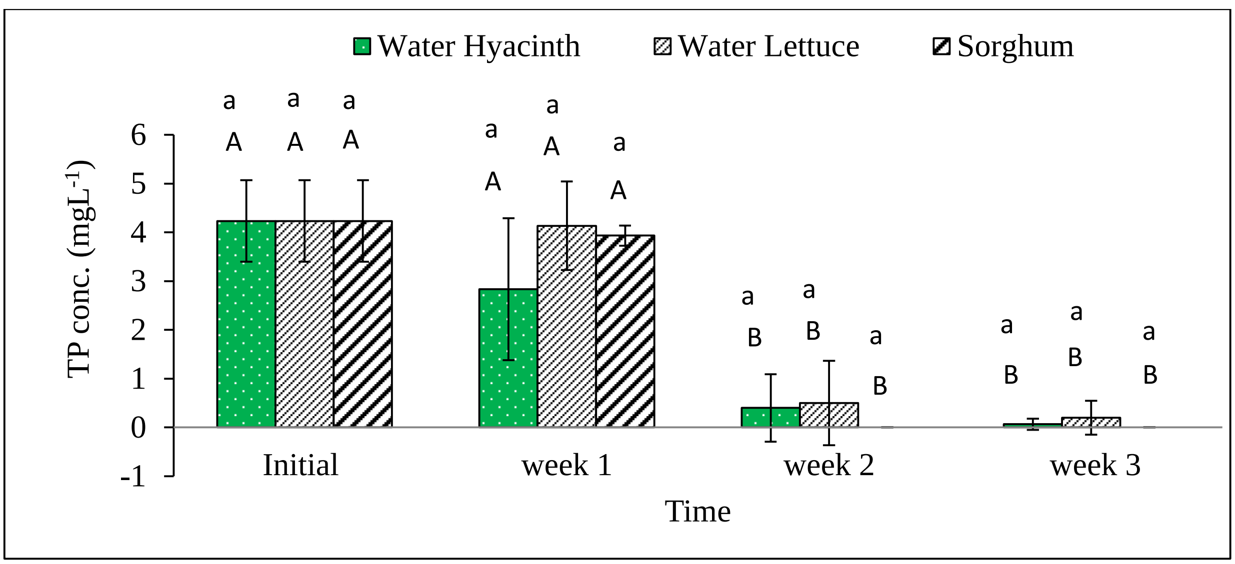

Figure 4.48. Total phosphorus concentration in the runoff (1:2) in the first batch experiment Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

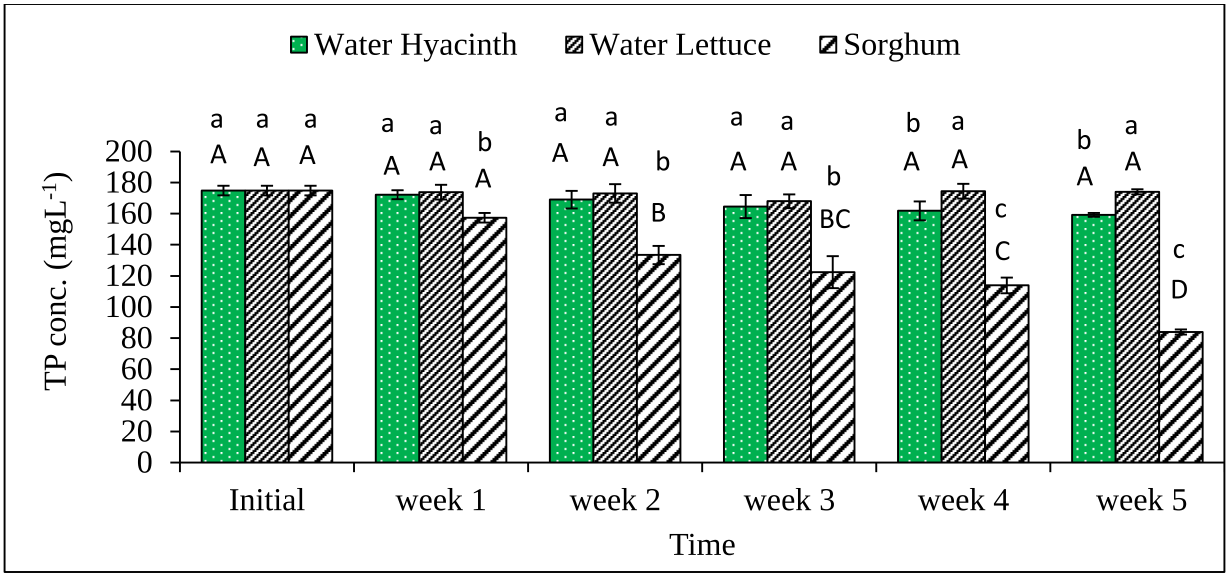

Figure 4.49. Total phosphorus concentration in the Hoagland solution in the second batch of experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

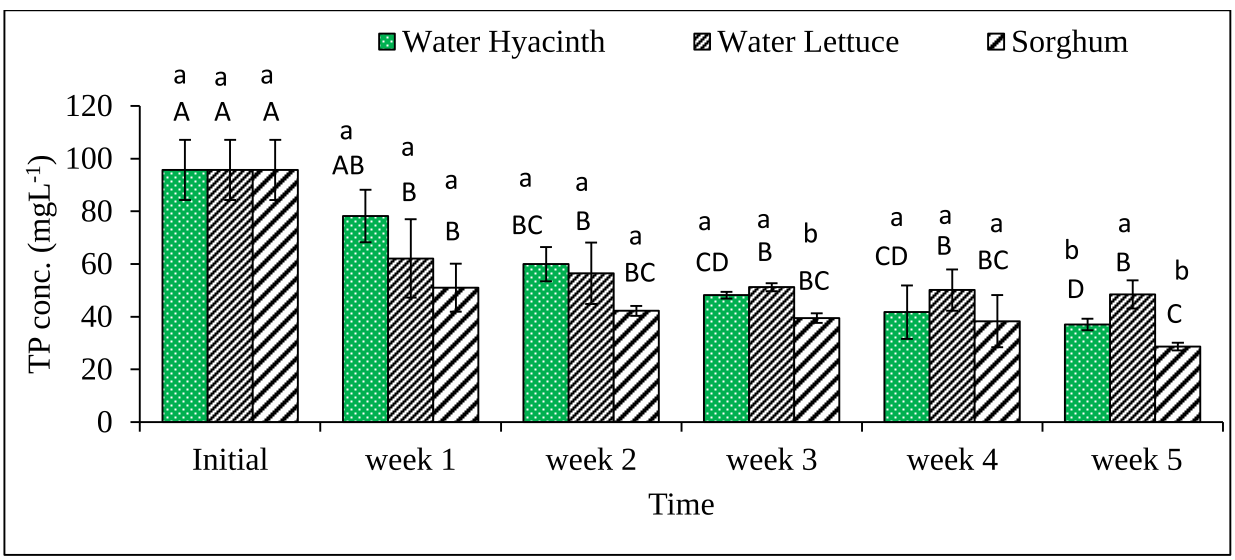

Figure 4.50. Total phosphorus concentration in the feedlot runoff (undiluted) in the second batch experiment. Bar with the same capital letter and the same plant type are not significantly different at each sampling week over the experiment period. Similarly, the same small letter for the same sampling date and different plants are not significantly different from each other at p≤0.05.

4.12. Overall nutrient percentage reduction

4.12.1. Overall nutrient percentage reduction by sorghum

In the first and second batch experiment, the TP reductions by sorghum from undiluted feedlot runoffs was almost 100% and 70%, respectively (Fig. 4.51 & 4.52). Similarly, for sorghum OP uptakes were approximately 90% and 70% in first and second batch experiments, respectively. The differences in TP uptake was due to the differences in initial TP concentrations in the feedlot runoff (collected from retention pond and immediate downstream of feedlot) and differences in initial plant densities. The NH_4-N uptakes by sorghum were close to 95% for both batches using undiluted feedlot runoff. The percentage reductions of TKN, NO_2-N+NO_3-N, and K from the feedlot runoff (undiluted) in the first batch experiment were approximately 60%, 75%, and 82%, respectively.

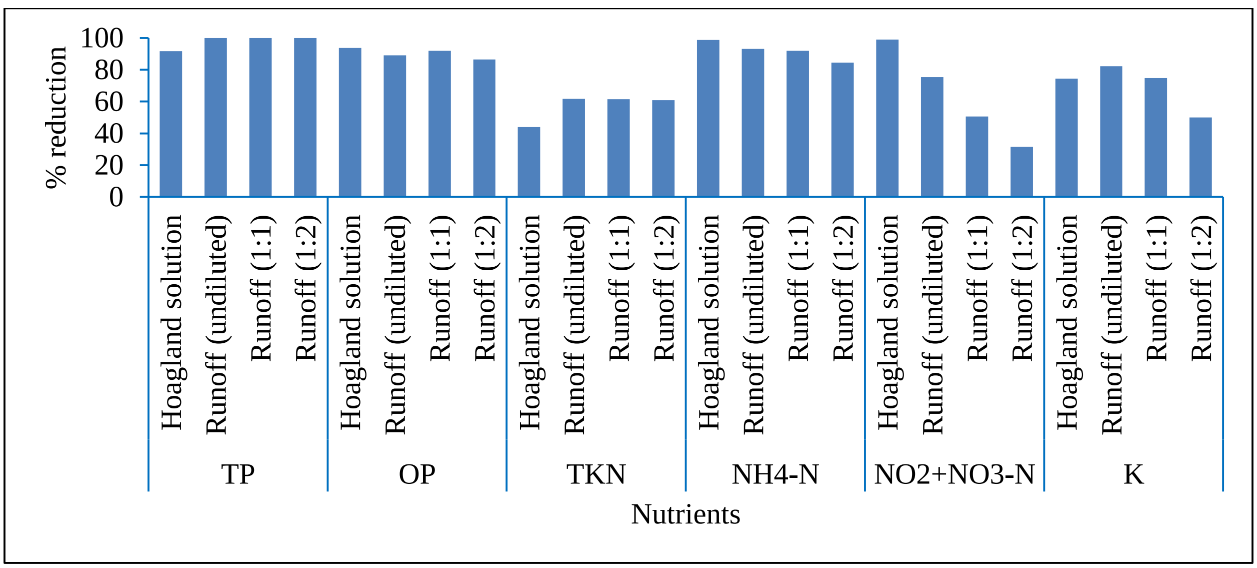

Figure 4.51. Overall nutrient percentage reduction by sorghum in the first batch experiment.

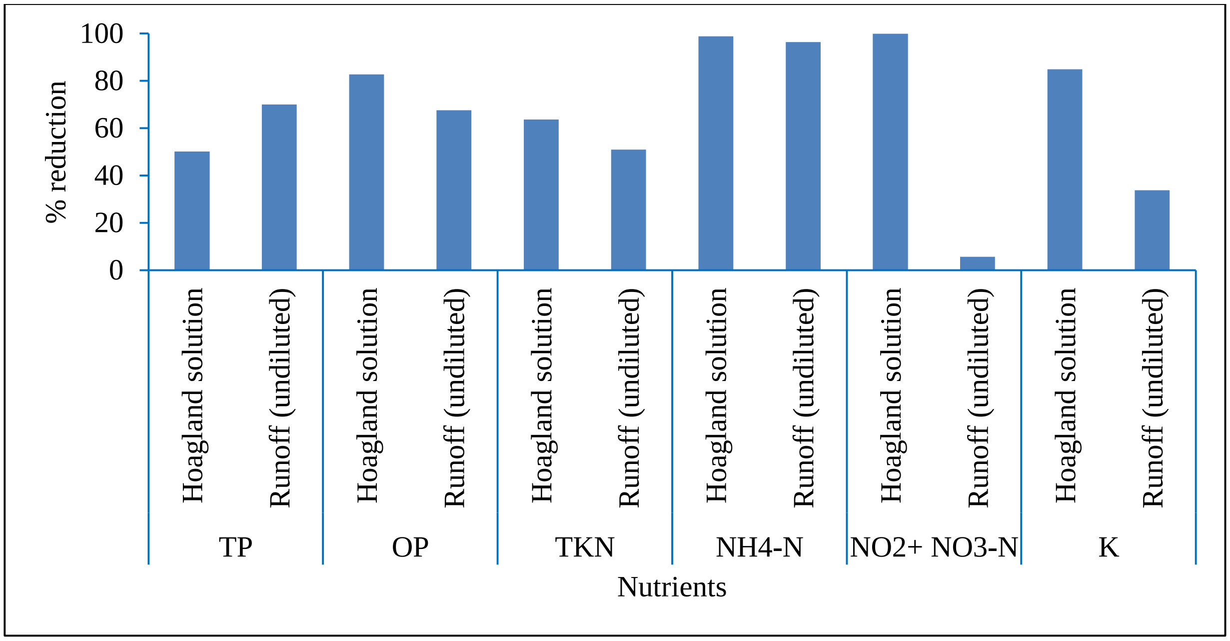

Figure 4.52. Overall nutrient percentage reduction by sorghum in the second batch experiment.

Similarly, percentage reduction of TKN was about 50%, potassium was less than 40%, and NO_2-N+NO_3-N was almost 10%, in second batch of feedlot runoff. In the first batch, percentage reductions of TP and OP by sorghum were more than 90%, and NH_4-N and NO_2-N+NO_3-N were close to 100% in Hoagland solution (Fig. 4.51). Similarly, for the same solution and same experiment with sorghum, the percentage reduction of K and TKN were approximately 75% and 45%, respectively. In second batch experiment, percent reduction of NH_4-N and NO_2-N+NO_3-N were nearly 100%, OP and K>80%, and TKN and TP were 60% and 50%, respectively, in Hoagland solution.

4.12.2. Overall nutrient percentage reduction by water hyacinth

In first batch experiment with feedlot runoff, the percentage reduction of NH_4-N was > 90%; TP, OP, TKN, and K were nearly 70%; and NO_2-N+NO_3-N reduction was less than 40% (Fig. 4.53). In the second batch experiment, water hyacinth showed the highest percent of NH4-

N reduction (~ 95%) followed by TKN and TP (~ 60%), and K (> 20%) from the feedlot runoff (undiluted). In the second batch experiment, the reduction of NO_2-N+NO_3-N, and OP were negative in feedlot runoff likely due to nitrification process and release of OP from the TP (Fig. 5.54). In the first batch experiment with Hoagland solution, OP and NH_4-N reduction were ~ 90%. The K, TP, and NO_2-N+NO_3-N reduction in Hoagland solution were about 50%, 33%, and 30%, respectively (Fig. 4.53). Similarly, in second batch with Hoagland solution experiment, NH_4-N removal was nearly complete followed by TKN (~ 60%). With the Hoagland solution in the second batch experiment, the K, OP, NO_2-N+NO_3-N and TP percentage reduction were below 50% and its reduction percentage values were 40%, 30%, 25%, and 5%, respectively (Fig. 5.54).

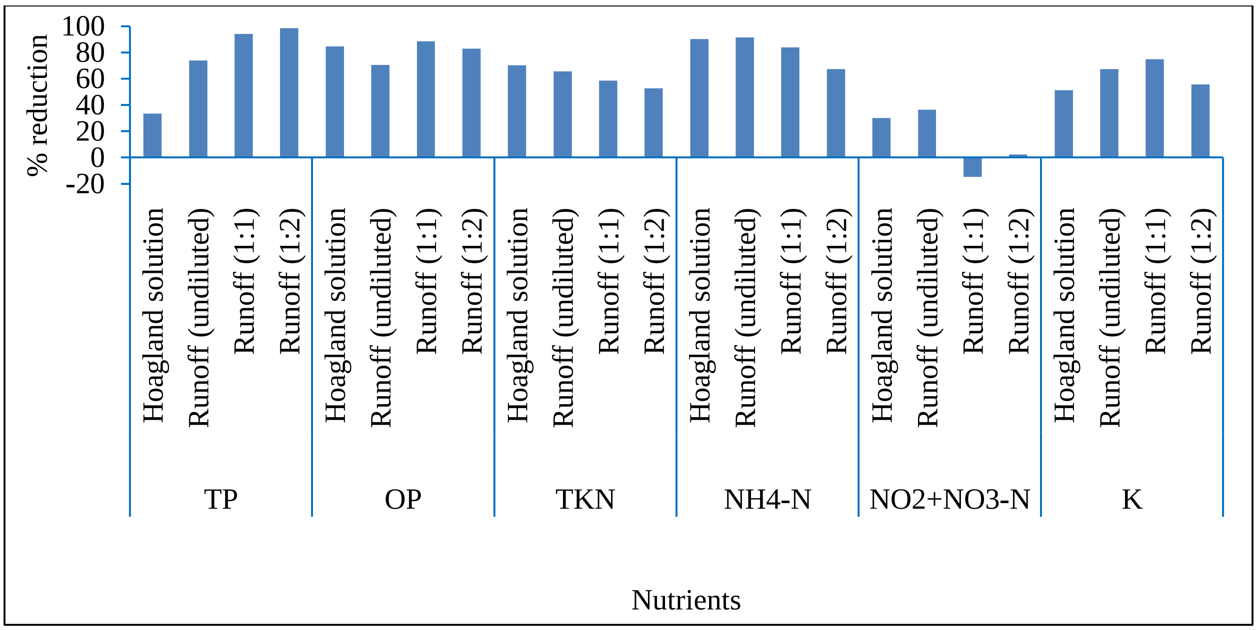

Figure 4.53. Overall nutrient percentage reduction by water hyacinth in the first batch experiment.

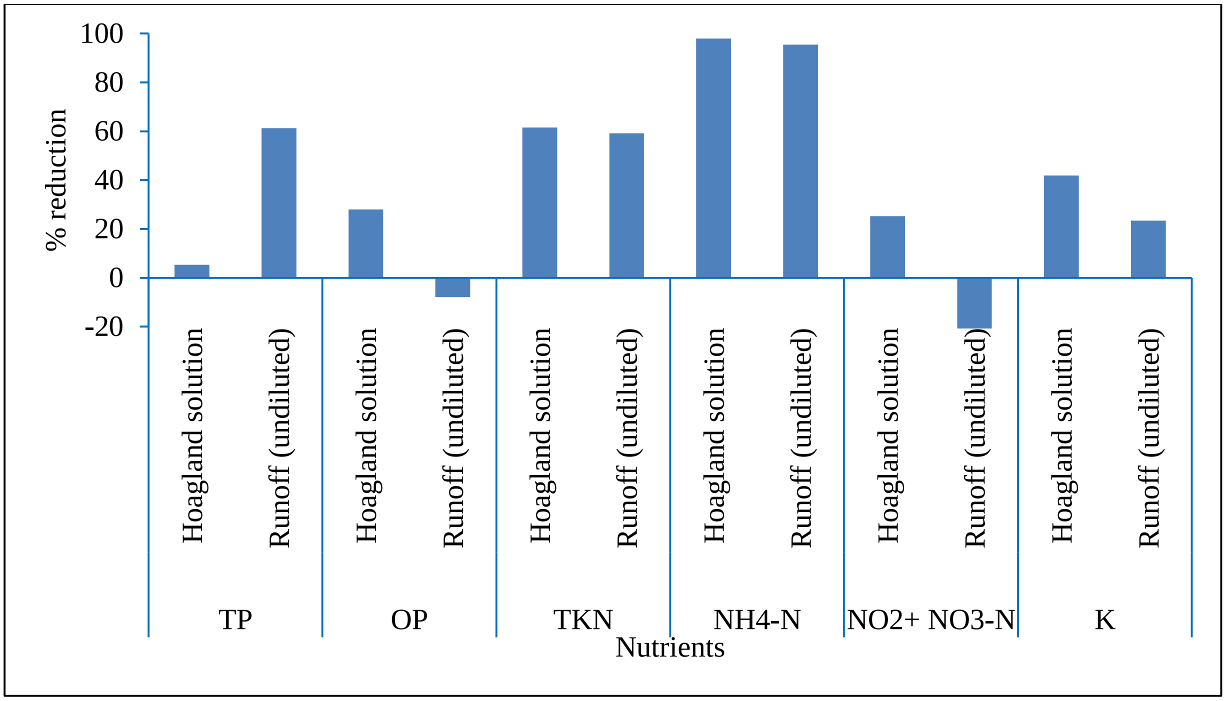

Figure 4.54. Overall nutrient percentage reduction by water hyacinth in the second batch experiment.

4.12.3. Overall nutrient percentage reduction by water lettuce

In first batch experiment with undiluted runoff, TP and NH_4-N removal by water lettuce were more than 90% (Fig. 4.55). Similarly, OP and NO_2-N+NO_3-N removal were more than 85%, TKN was more than 70% and K was reduced only about 25% from the feedlot runoff (Fig. 4.55). In second batch experiment, the NH_4-N reduction was highest (95%) and K reduction was lowest (20%) among other nutrients in feedlot runoff. The TKN, OP, and TP were reduced about 60%, 57% and 50% from the feedlot runoff, respectively (Fig. 4.56). The 16% increase in NO_2-N+NO_3-N in feedlot runoff was due to the nitrification process (Fig. 4.56).

In first batch experiment with Hoagland solution, water lettuce showed highest uptake of NH_4-N and OP nutrients (approximately 85% NH_4-N and 75 % OP). The rest of the nutrients were reduced less than 50%. The percent reduction of K, TKN, NO_2-N+NO_3-N, and TP were about 40%, 35%, 20% and 12% in Hoagland solution, respectively (Fig. 4.55). Similarly, in second batch experiment with Hoagland solution, the nutrient reduction was very low as compared to the first batch with Hoagland solution because plants could not grow properly due to infestation of diseases. The NH_4-N and TKN concentration were reduced about 40%. The K, OP and NO_2-N+NO_3-N percentage reduction were about 17%, 10% and 5% from the Hoagland solution, respectively but TP did not reduced at all (Fig. 4.56).

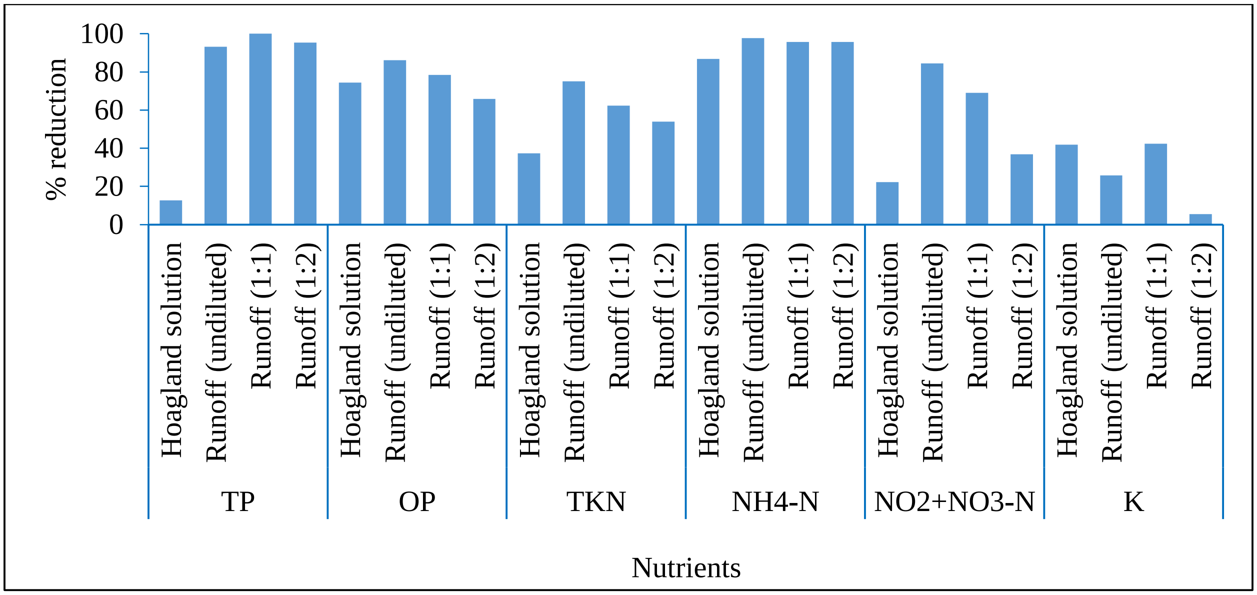

Figure 4.55. Overall nutrient percentage reduction by water lettuce in the first batch experiment.

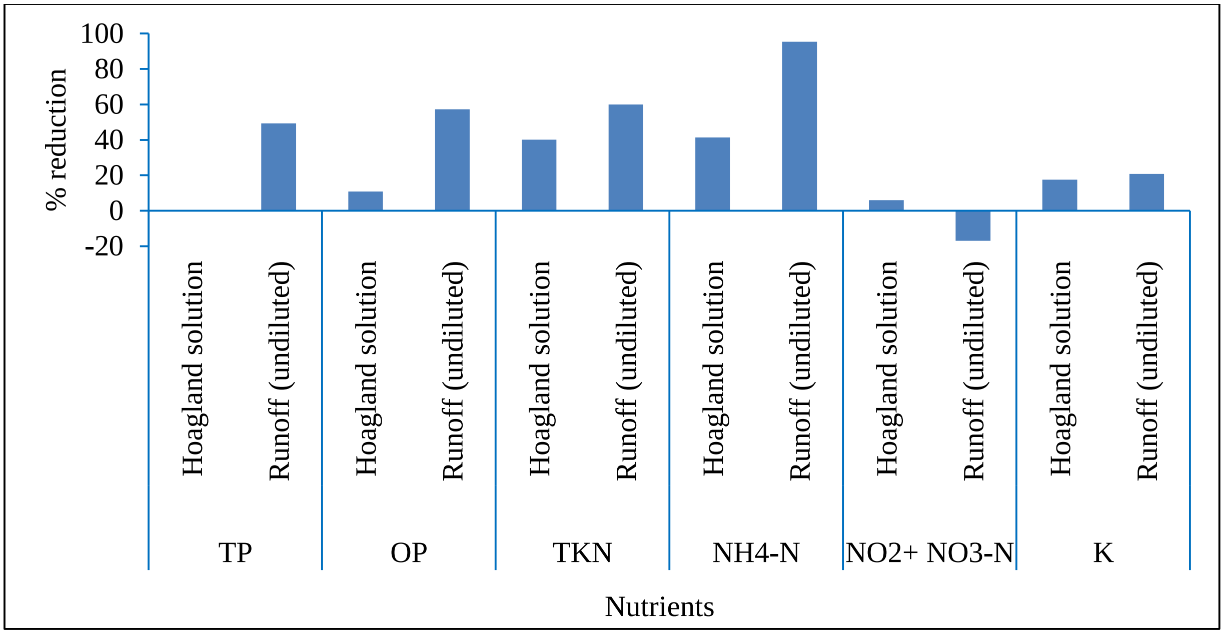

Figure 4.56. Overall nutrient percentage reduction by water lettuce in the second batch experiment.

In summary, sorghum outperformed water hyacinth and water lettuce and reduced most of the nutrients much quicker than other plants grown in this hydroponics studies. The negative reduction of some of the nitrogen based nutrients were due to the nitrification and ammonification process; and phosphorus based nutrient was due to the releasing of soluble phosphorus from the TP mainly in feedlot runoff under hydroponic condition. The net plants biomass in these experiments also revealed that the Hoagland solution contains all of the required nutrients for plants grown in this study. The experiment also concluded that plants can be grown up in feedlot runoff as-is condition, although it is not available balanced nutrient. All plants were able to reduce noticeable amount of nutrient by up taking nutrients, thus these plants may be grown to feedlot runoff collection pond or runoff treatment area to reduce runoff nutrient contribution.

4.13. Elemental analysis of plants grown in feedlot runoff and Hoagland solution

The results obtained from the elemental analysis of plants tissue in the first batch are shown in the Table 4.5 and second batch are shown in the Table 4.6. In first batch, the series of feedlot runoff dilution were made and plants were grown in that feedlot runoff. From the water sample, elements such as B, Cu, Mg, Mn, Mo, P, S, Zn and Fe concentration were higher in plants tissue which were grown in feedlot runoff (undiluted) than the plants grown in feedlot runoff (1:1 & 1:2). However, Mo and Zn concentration were higher in water hyacinth and S was higher in sorghum grown in feedlot runoff (1:1 & 1:2) than plant grown in feedlot runoff (undiluted). From the ICP analysis, Na^+ concentration was higher in all plants tissue that was grown in feedlot runoff than the plant grown in the Hoagland solution and this could be the plant adjustment towards the high salinity condition. It was also shown that higher the dilution of feedlot, more Na^+ concentration in all plant tissues as shown in Table 4.5. The probable reason for higher Na^+ accumulation in plant tissue was for the ionic balance. When the feedlot runoff was diluted, the nutrient concentration, especially nitrogen concentration decreased. These decreased nitrogen concentration was almost insufficient for plants' growth. Instead of NH_4^+ uptake in replacement of H^+, plant might uptake Na^+ from the solution. The increasing order of Na^+ present in the plant tissue seeded in decreasing concentration of feedlot runoff was ionic balanced by up taking decreasing order of K^+. According to Turhan and Eris (2005) higher Na^+ uptake by plants means lower K^+ uptake by plants because Na^+ is the competitive ions for K^+. From the water sample analysis, it was found that the amount of K uptake by the plants was decreased due to the dilution of feedlot sample (Figs. 4.34 to 4.36). It also verified that Na^+ remarkably hinder the K^+ uptake. It is also found that high Na^+ present in the solution also hinder the uptake of Ca^{2+} in the plant tissues (Hu & Schmidhalter, 2005) which was shown true for all of the plants grown in undiluted and diluted feedlot runoff as shown in Table 4.5.

The concentration of Mo, S and Zn were higher, Ca and Mn concentration were almost the same, and B, Cu, Mg, Na and Fe concentrations were lower in initial Hoagland solution than initial feedlot runoff (also shown in Table 4.7). From the elemental analysis of plants tissue, B, Ca, Cu, Mo, P and Zn concentration were higher in plant which were grown in the Hoagland solution than the plants grown in feedlot runoff in both experiment. Except Mg and S concentrations in sorghum plant in the first batch and Mn concentration in water hyacinth plant in the second batch, the concentrations of Mg, Mn, Na, S and Fe were higher in plants which were grown in feedlot runoff than plants grown in Hoagland solution (also shown in Table 4.5 and 4.6).

Table 4.5. ICP analysis results of plants' tissue grown in the feedlot and Hoagland solution in the first batch experiment.

Element mg kg-1 dry weight	B	Ca	Cu	Mg	Mn	Mo	Na	P	S	Zn	Fe
Water Hyacinth in Hoagland solution	41.85	20131	25.33	5341	227.6	12.64	3571	12110	4487	163.9	454
Water Hyacinth in feedlot runoff (undiluted)	28.84	17620	22.64	10188	479.1	0.68	5229	5031	5587	30.3	2095
Water Hyacinth in feedlot runoff (1:1)	22.59	14102	28.54	10506	218.2	0.88	9829	4219	5455	31.7	1366
Water Hyacinth in feedlot runoff (1:2)	21.57	12896	16.26	10097	190.0	1.16	11087	3697	5773	47.5	666
Water Hyacinth in Hoagland solution	45.21	15914	25.79	3678	150.8	6.24	3918	8828	5172	248.9	200
Water Hyacinth in feedlot runoff (undiluted)	44.25	20465	13.69	9488	623.1	0.92	10736	3727	3448	55.2	1546
Water Hyacinth in feedlot runoff (1:1)	43.92	15914	13.01	7724	329.4	0.72	11446	2983	3268	37.9	1145
Water Hyacinth in feedlot runoff (1:2)	40.54	15876	12.35	7326	211.2	0.60	14437	2722	2707	34.7	724
Water Hyacinth in Hoagland solution	59.29	7710	7.09	4045	78.4	1.80	802	5219	2430	41.6	367
Water Hyacinth in feedlot runoff (undiluted)	34.32	20567	16.11	9816	377.1	<MDL	3450	3809	3380	40.9	5917
Water Hyacinth in feedlot runoff (1:1)	34.39	9631	9.98	6772	179.4	0.68	3514	3765	5157	27.3	1611
Water Hyacinth in feedlot runoff (1:2)	36.54	10896	14.78	7477	188.6	<MDL	3522	3094	5396	41.7	2081

Table 4.6. ICP analysis results of plants' tissue grown in the feedlot and Hoagland solution in the second batch experiment.

Element mg kg-1 dry weight	B	Ca	Cu	Mg	Mn	Mo	Na	P	S	Zn	Fe
W. Hyacinth at initial	21.70	14291	15.70	5685	32.2	1.72	11336	9025	5012	16.23	126
W. Hyacinth grown in feedlot runoff	32.72	12867	12.67	10119	420.3	1.28	7931	5936	8135	109.97	554
W. Hyacinth grown in Hoagland solution	27.64	10508	32.27	6116	223.4	25.15	3192	13279	4591	165.85	300
Water Lettuce at initial	40.76	23271	14.88	6586	47.8	4.43	15365	6330	6847	24.51	306
Water Lettuce grown in feedlot runoff	37.04	12510	12.26	10553	701.4	2.04	9984	6069	6780	89.82	2979
Water Lettuce in Hoagland solution	46.74	24006	91.18	5828	359.5	41.16	3289	8282	5614	1567	749
Sorghum at initial	16.80	18251	17.85	9631	237.1	0.91	7972	2716	4152	45.80	4287
Sorghum grown in feedlot runoff	23.82	6881	9.68	5494	192.8	0.44	2394	5123	3635	53.84	1497
Sorghum grown in Hoagland solution	33.57	9822	13.32	7088	124.9	5.19	1776	8674	4476	64.95	388

4.14. Elemental analysis of the feedlot runoff and Hoagland solution in the second batch experiment

For the elemental analysis of feedlot and the Hoagland solution, water samples were taken at the beginning and at the end of hydroponics experiment. From the elemental analysis of water samples, it was found that initial concentration of B, Cu, Mg, Na and Zn were higher, Ca and Mn were almost same, and Mo, S, and Zn were lesser in feedlot runoff (undiluted) than the Hoagland solution. From the elemental analysis of feedlot runoff (undiluted) at the beginning and at the end of experiment, all three types of plants except B reduced most of the elements' concentration and Cu concentration did not reduced by sorghum. Similarly, from the elemental analysis of Hoagland solution, most of the element' concentrations were reduced by all three types of plants except Na was not reduced by all three types of plants and B was not reduced by sorghum plants which is also shown in Table 4.7.

Table 4.7. ICP analysis results of feedlot runoff and Hoagland solution before and after plants grown during the second batch experiment.

Element (mg L^{-1})	B	Ca	Cu	Mg	Mn	Mo	Na	S	Zn	Fe
Feedlot runoff (undiluted) at initial	0.32b ±0.009	106.3a ±3.28	0.02a ±0.01	118.6a ±2.43	0.58a ±0.068	0.01b ±0.006	208.7a ±4.62	245.4a ±5.72	0.06d ±0.026	2.43a ±0.592
Feedlot runoff (undiluted) in Water Hyacinth	0.29bc ±0.003	83.4c ±1.10	0.02ab ±0.01	97.6b ±0.66	0.03c ±0.015	0.01b ±0.001	205.3a ±1.70	224.2b ±2.48	0.03e ±0.006	0.78bc ±0.067
Feedlot runoff (undiluted) in Water Lettuce	0.29bc ±0.009	82.4c ±1.65	0.02abc ±0.005	100.1b ±2.80	0.05c ±0.028	0.01b ±0.004	207.7a ±8.85	228.8b ±9.62	0.03e ±0.005	0.65bc ±0.238
Feedlot runoff (undiluted) in Sorghum	0.43a ±0.047	82.7c ±3.47	0.03a ±0.006	97.9b ±2.45	0.01c ±0.011	0.01b ±0.004	202.9a ±2.29	220.0b ±7.47	0.04de ±0.009	1.07b ±0.129
Hoagland solution at initial	0.27c ±0.006	105.4a ±7.36	0.015bc ±0.002	26.9c ±0.69	0.58a ±0.016	0.024a ±0.001	17.4c ±0.50	39.6c ±4.00	0.28a ±0.02	0.82b ±0
Hoagland solution in Water Hyacinth	0.26c ±0.014	93.0b ±1.81	0.00d	20.5d ±0.61	0.31b ±0.042	0.00b	32.1b ±059	33.5c ±0.25	0.09c ±0.037	0.07cd ±0.017
Hoagland solution in Water Lettuce	0.28c ±0.003	96.9b ±3.70	0.01cd ±0.001	24.9c ±0.45	0.28b ±0.162	0.02a ±0.001	30.9b ±0.70	37.3c ±1.14	0.15b ±0.009	0.07cd ±0
Hoagland solution in Sorghum	0.41a ±0.016	49.07d ±3.049	0.004d ±0	0.64e ±0.199	0.005c ±0	0.00b	30.03b ±0.509	16.9d ±2.436	0.002e ±0	0.00d

CHAPTER 5. RESULT AND DISCUSSION OF ELECTROLYSIS

5.1. Background of electrolysis experiment

5.1.1. Initial concentration of the feedlot runoff nutrients

The feedlot runoff was collected from the North Dakota State University's Beef Research Centre, Fargo, North Dakota. Before starting treatment process, the runoff sample used was mixed thoroughly in a bucket and subsample was collected to set-up experiment. The experiment was conducted in batches and there were 27 experimental units in total. From each experimental unit, sample was collected and analyzed and their average initial concentrations are listed in Table 5.1.

Table. 5.1. Initial characteristics of the feedlot runoff in electrolysis experiment.

Parameter	Initial concentration
Number of samples	27
pH	8.02±0.229
Conductivity ($mScm^{-1}$)	3.60±0.30
TN (mgL^{-1})	32.86±4.17
TP (mgL^{-1})	49.59±6.52
COD (mgL^{-1})	263.52±19.50
TS (mgL^{-1})	3.06±0.28

5.2. pH change in the feedlot runoff due to electrolysis

In most of the cases, after electrolysis, the pH of the electrolysis solution were increased, but the differences were not significant except iron electrodes (Fig.5.1). The increased pH in electrolysis solution was likely due to the excess of hydroxyl ions produced at the cathode and liberation of free OH^- (Dalvand et al., 2011; Feng et al., 2007). In this experiment, pH of iron electrodes treated runoff was the highest, and hybrid electrodes treated runoff had the lowest. Al-Al electrode treated runoff resulted in between these two types of electrodes. It is also evident from Figure 2 that applied voltage does not have any effect on pH changes except aluminum electrodes for all applied voltages.

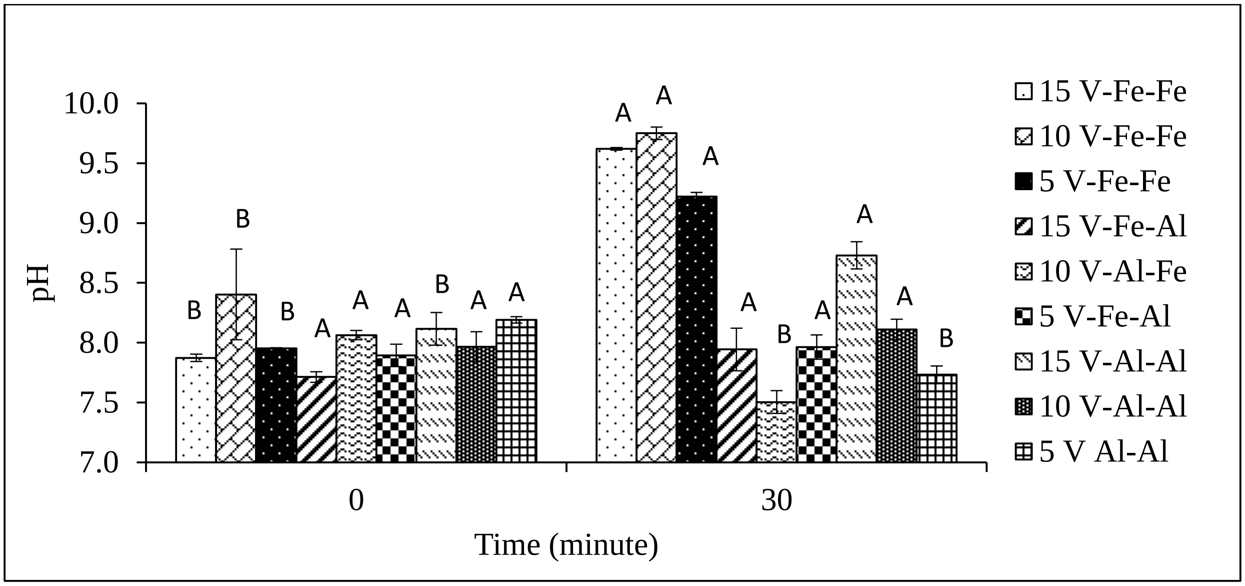

Figure 5.1. pH of the feedlot runoff at start and end of electrolysis by different electrodes. Bar with the same capital letter and the same electrode with the same applied electrode potential are not significantly different over experiment period at $p \leq 0.05$.

5.3. Electrical Conductivity change in the feedlot runoff due to electrolysis

This study demonstrated that after electrolysis the EC of feedlot runoff decreased significantly by all types of electrodes. The highest EC reductions (6.1% for Fe-Fe, 13.3% for Al-Al, and 18.98% for Al-Fe) were observed at a 15 V applied electrode potential followed by 10 V (5.56% for Fe-Fe, 8.11% for Al-Fe, 9.72% for Al-Al) and 5 V (3.6% for Fe-Fe, 2.96% for Al-Fe, and 5.83% for Al-Al).

The Al- Fe electrodes at 15 V resulted in the highest EC reduction when compared with Fe-Fe and Al-Al electrodes for 30 minutes electrolysis (Fig. 5.2). On the contrary, at 10 V and 5

V applied electrical potential with 30 minutes electrolysis; Al-Al electrodes reduced more EC than Fe-Fe and Al-Fe electrodes (Fig. 5.2). The changes in EC of the solution were occurred by the free ions present in the solution. After electrolysis, the electrostatic charge of dispersed particles present in the solution are neutralized and thus the electrical conductivity of the solution is reduced (Kılıç & Hoşten, 2010). Tchamango et al. (2010) also mention that by means of electrolysis process, EC could be decreased due to the consumption of protons by transformation of phosphoric acid into solid metal phosphate

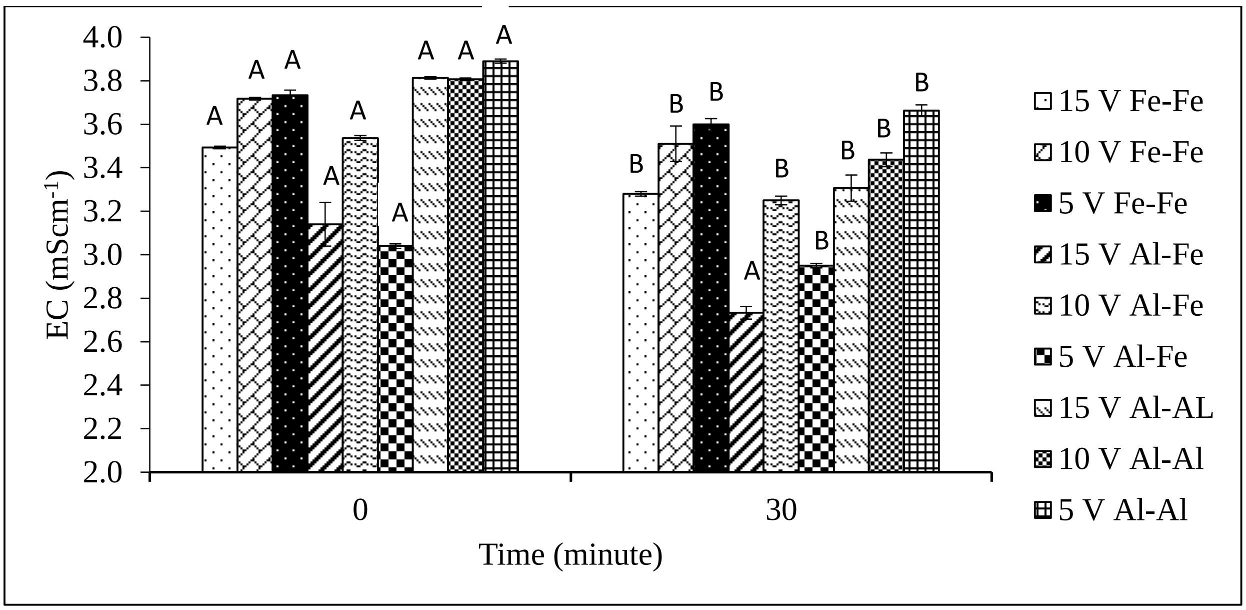

Figure 5.2. Electrical conductivity value of feedlot runoff due to electrolysis by different electrodes. Bar with the same capital letter and the same electrode with the same applied electrode potential are not significantly different over experiment period at $p \leq 0.05$.

5.4. Total Phosphorus (TP) reduction due to electrode and time

In this experiment, TP reduction was 100% by all electrodes combination and at all the applied electrical potential differences within 30 minute of treatment time. At 15 V, 10 V, and 5 V applied electrode potentials, about 100% TP reduction were measured within 3 to 5 minutes, 3 to 10 minutes and 8 to 10 minutes treatment time depending on the electrode combination, respectively (Figs. 5.3, 5.4 & 5.5). These results show that TP reductions increased with increased electrical potentials for all electrodes combination. At 15 V applied electrical potential, TP concentration reduced significantly for all types of electrode compared to the initial TP concentration. It took about three minutes to reduce TP about 100% by the Fe-Fe electrodes, whereas it took five minutes for Al-Al and Fe-Fe electrodes to achieve at that reduction level. After that, the TP reductions were not significant among electrodes, since the maximum reduction occurred already within that time (Fig. 5.3). For 10 V applied electrical potential, TP concentration reduced about 100% within five minutes for Fe-Fe and within 8-10 minutes for the Al-Fe and Al-Al electrodes, respectively (Fig. 5.4). At 10 V, electrode potential, Al-Al and Fe-Fe electrodes reduced significantly higher amount of TP than the Al-Fe electrodes at three minute of electrolysis, but after 10 minute of electrolysis, all of the electrodes combination reduced the maximum TP (Fig. 5.4). Similarly, for 5 V applied electrode potential, it took longer time to reduced TP concentration significantly (Fig. 5.5). Overall, Al-Al and Fe-Fe electrodes performed the best.

The TP reductions were mainly due to the production of Al or Fe ions in anode. The hydroxide ion produced in cathode is immediately react with metal ions in aqueous medium and to produce metallic hydroxides. Subsequently, this process initiated polymerization reactions when metallic hydroxide particles produced had reached sufficient concentration and deposited as sediment and thus decrease amount of total phosphorus from the solution (Dinh-Duc et al., 2014; Ilhan et al., 2008; Inan & Alaydin, 2014; Laridi et al., 2005).

Overall, after 5 minutes of electrolysis time, there were no significance difference in TP reduction by electrode types for 15 V applied potential. Similarly, after 10 minutes of electrolysis time, there were no significance difference in TP reduction by electrode types for 10 V and 5 V applied electrode potential. Al-Al and Fe-Fe electrodes were significantly reduced TP than Al-Fe electrode for 15 V and 10 V applied potential during 3 minutes of electrolysis time and for 5 V applied potential during 8 minutes of electrolysis time. Overall, Al-Al electrodes shown better TP removal for all electric potential during the experimental period (Figs. 5.3, 5.4 & 5.5).

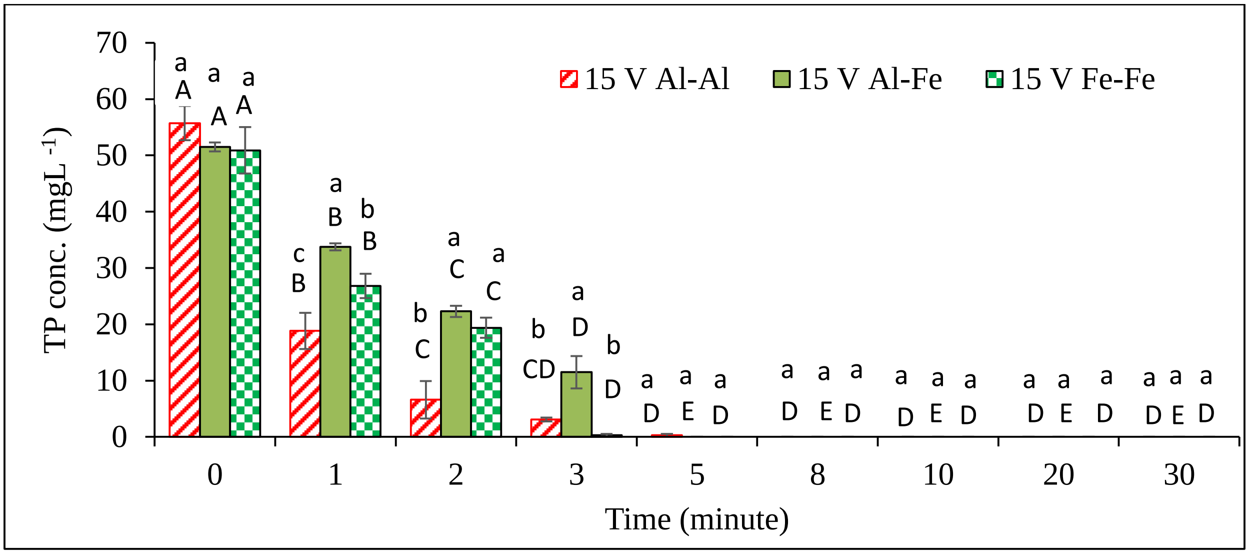

Figure 5.3. Total phosphorous value due to 15 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

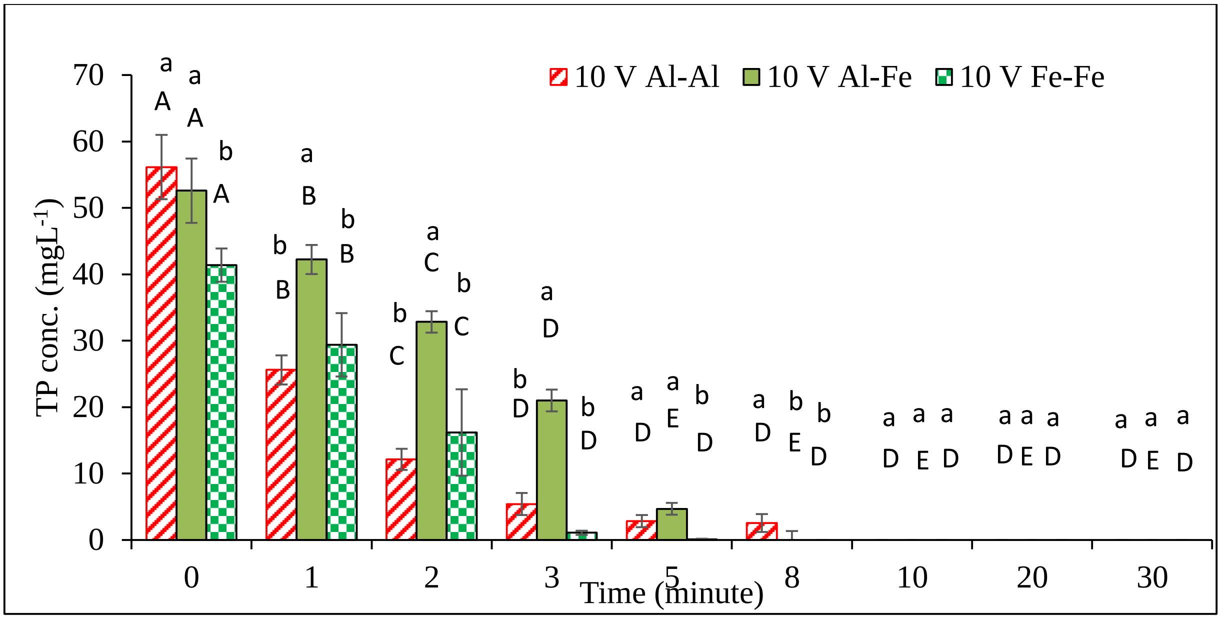

Figure 5.4. Total phosphorous value due to 10 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

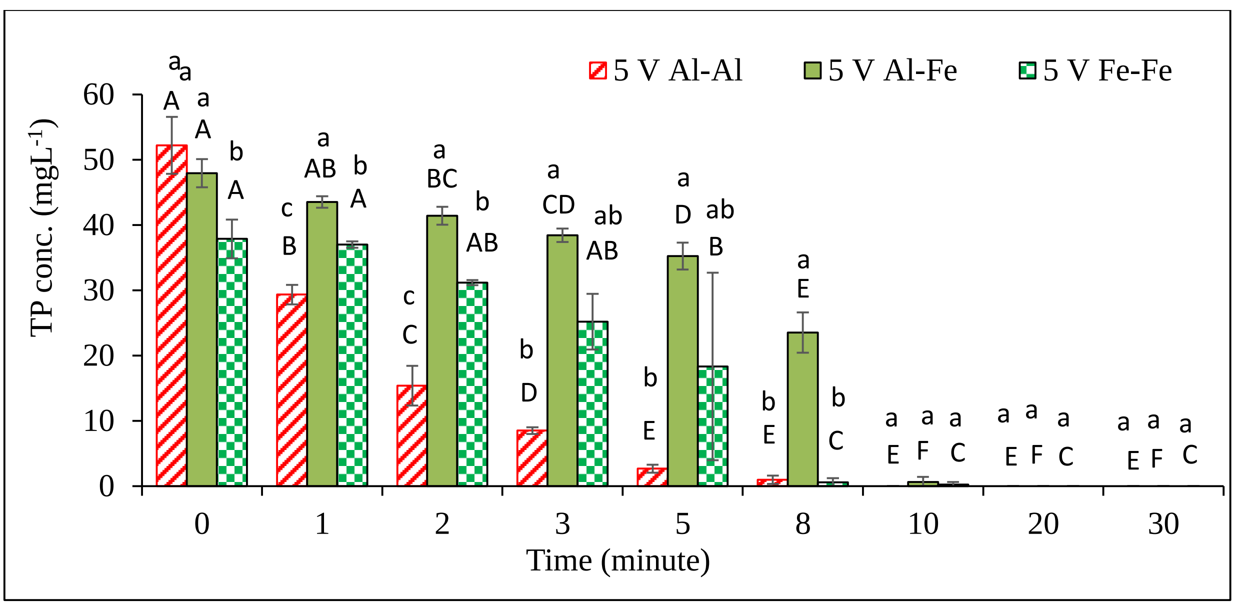

Figure 5.5. Total phosphorous value due to 5 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

5.5. Total Nitrogen (TN) reduction due to electrode and time

In electrolysis experiment, the TN concentration reduction was shown by all type of electrode combination and at all applied potential levels. The TN reduction at 15 V electrical potential were the highest compared to at 10 V and 5 V applied electrode potential for all types of electrodes at 30 minutes electrolysis time (Figs. 5.6, 5.7 & 5.8). At 15 V applied electrical potential and 30 minutes electrolysis time, TN reduction were approximately 63%, 56%, and 41% for Al-Fe, Al-Al and Fe-Fe electrodes, respectively (Fig. 5.6). Similarly, at 10 V potential and 30 minutes electrolysis, the TN reductions were approximately 47%, 42%, and 38% for Al-Al, Al-Fe and Fe-Fe electrode, respectively (Fig. 5.7). However, at 5 V for the same electrolysis time, Fe-Fe resulted in the lowest TN reduction (Fig. 5.8). The TN reduction at 5 V by the Al-Al, Al-Fe and Fe-Fe electrodes were about 45%, 38%, and 27% by, respectively for 30 minutes electrolysis time (Fig. 5.8).

Overall, Al-Fe electrodes outperformed Al-Al and Fe-Fe electrodes at all voltages in reducing TN from the feedlot runoff. At 15 V applied electrode potential, Al-Fe electrodes reduced significantly greater amount of TN than the Al-Al and Fe-Fe electrodes (Fig. 5.6). Similarly, with 10 V potential, Al-Al electrodes reduced significant amount of TN than the Al-Fe and Fe-Fe electrode (Fig. 5.7). For 5 V electrode potential, Al-Fe and Al-Al reduced significant amount of TN than the Fe-Fe electrode (Fig. 5.8). Therefore, any of the electrodes combination may be used in reducing TN, but Al-Al and Al-Fe combination performed the best at greater voltage potential.

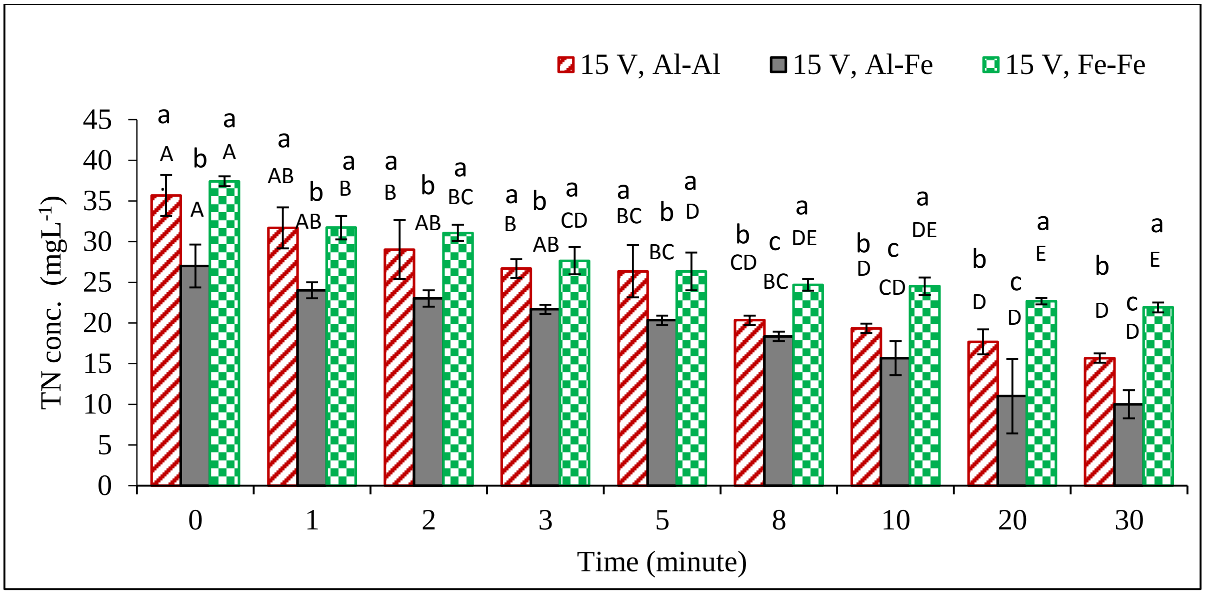

Figure 5.6. Total nitrogen value due to 15 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

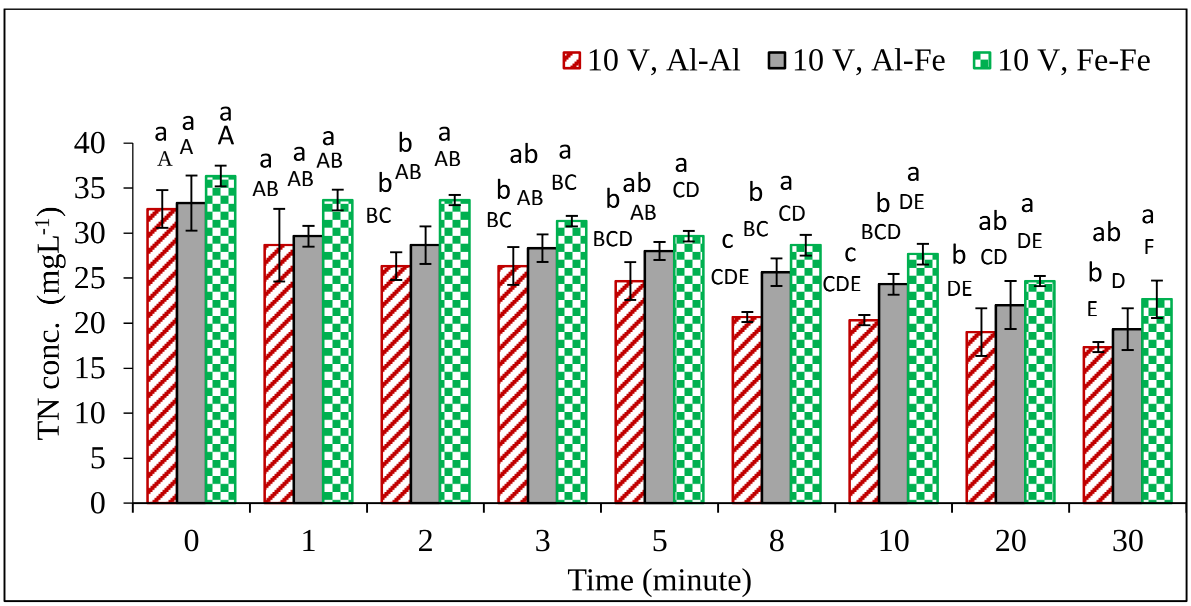

Figure 5.7. Total nitrogen value due to 10 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

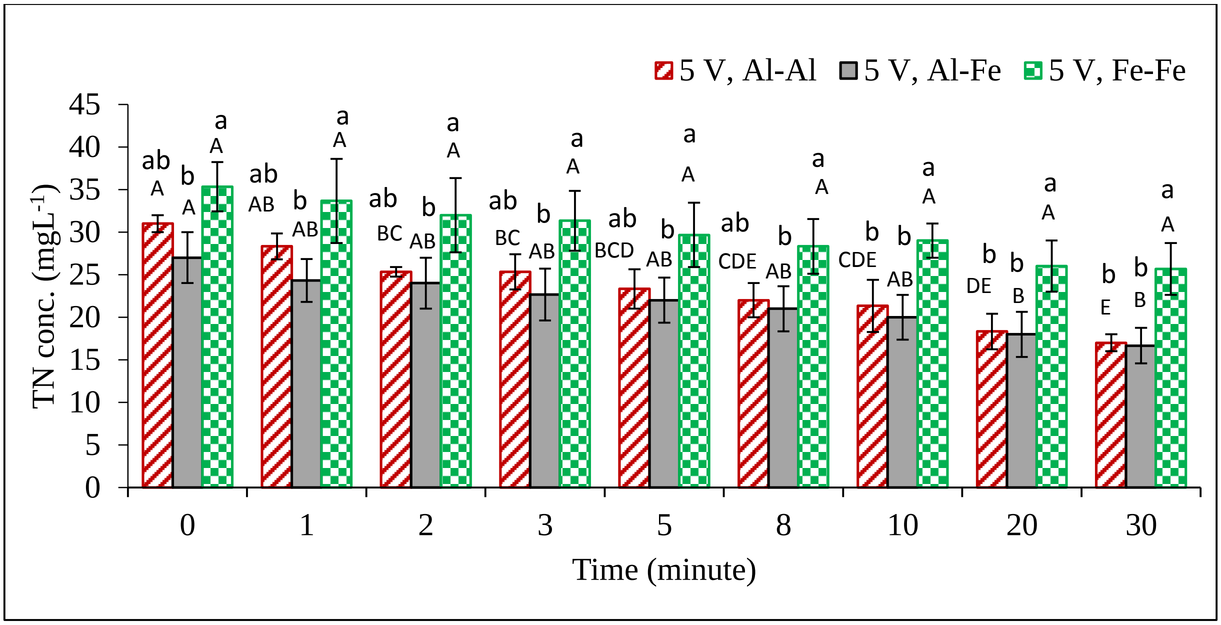

Figure 5.8. Total nitrogen value due to 5 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

5.6. Chemical Oxygen Demand (COD) change due to electrode and time

During the electrolysis, researcher applied three different voltage and 15 V applied electrode potential reduced the highest percentage of COD than 10 V and 5 V. Higher electrical potential directly related to the liberation of higher amount of metal ions to the runoff. At 15 V potential, the percentage reduction of COD were about 78% by all the electrodes at 30 minutes of electrolysis time as shown in Figure 5.9. Similarly, at 10 V applied electrode potential, the percentage reduction of COD were approximately 73, 68, and 67% at 30 minutes treatment time by Al-Al, Al-Fe and Fe-Fe electrodes, respectively (Fig. 5.10). Likewise, at 5 V applied electrical potential for the same treatment time, the percentage reduction of COD were 66%, 58%, and 53% for Al-Al, Al-Fe and Fe-Fe electrodes, respectively (Fig. 5.11).

At 15 V applied electrode potential level, the COD concentration reduced gradually throughout the experimental time and COD concentration reduced significantly within one minute of EC process and continued to reduce. However, there were no significance differences in COD reduction among electrode types throughout the experiment (Fig 5.9). For 10 V applied electrode potential level at 30 minutes electrolysis time, Al-Al electrode combination resulted in the maximum reduction, but the differences were not significant with other electrodes combination (Fig. 5.10). Similarly, at 5 V applied electrical potential level, the COD reduction was significantly different by Al-Al electrode than Al-Fe and Fe-Fe electrodes (Fig 5.11).

Overall, at 15 and 10 V applied electrode potential and at 30 minutes electrolysis time, COD reductions were not significantly different among electrodes (Figs. 5.9 & 5.10), but, at 5 V applied electrode potential level, Al-Al electrodes reduced COD significantly higher than other electrodes (Fig. 5.11). Therefore, all electrodes were capable of reducing COD, but Al-Al electrodes resulted in the best performance in any electrical potential.

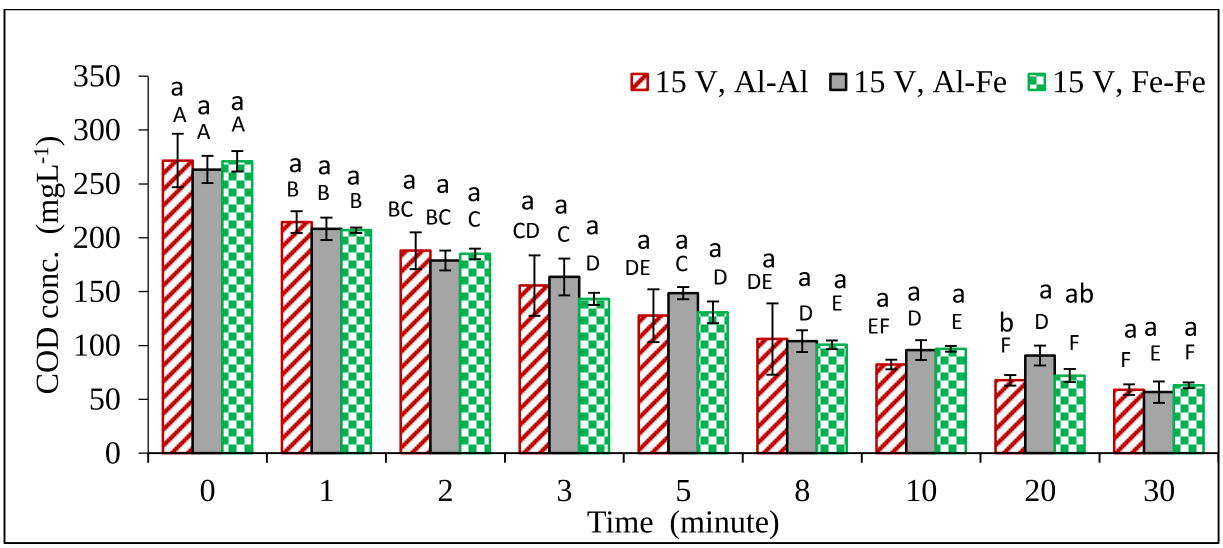

Figure 5.9. COD value due to 15 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

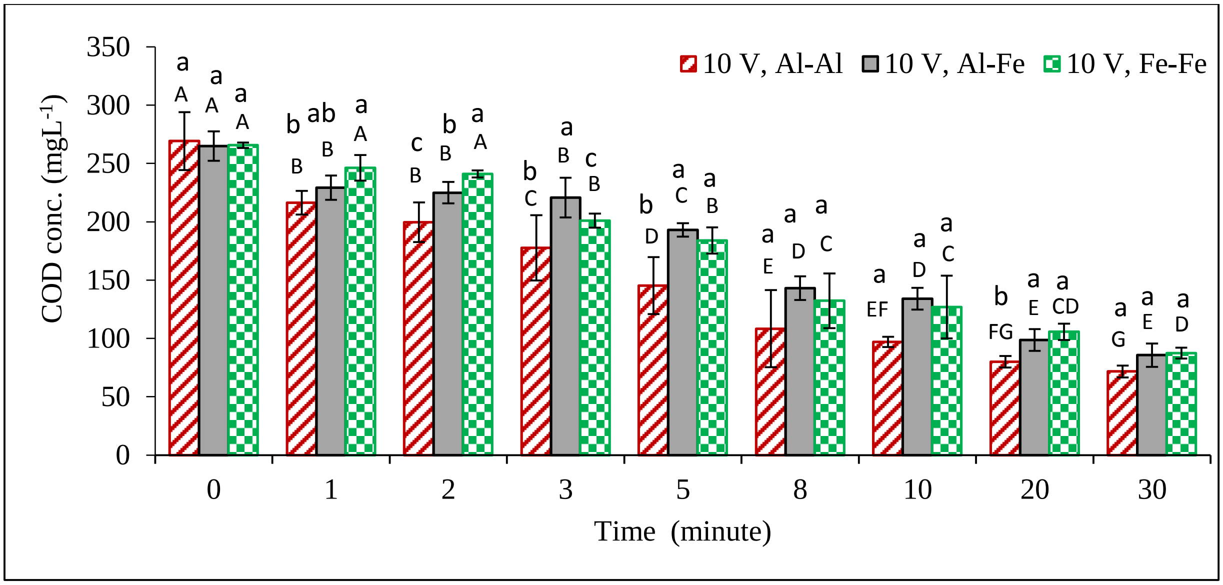

Figure 5.10. COD value due to 10 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different from each other at p≤0.05.

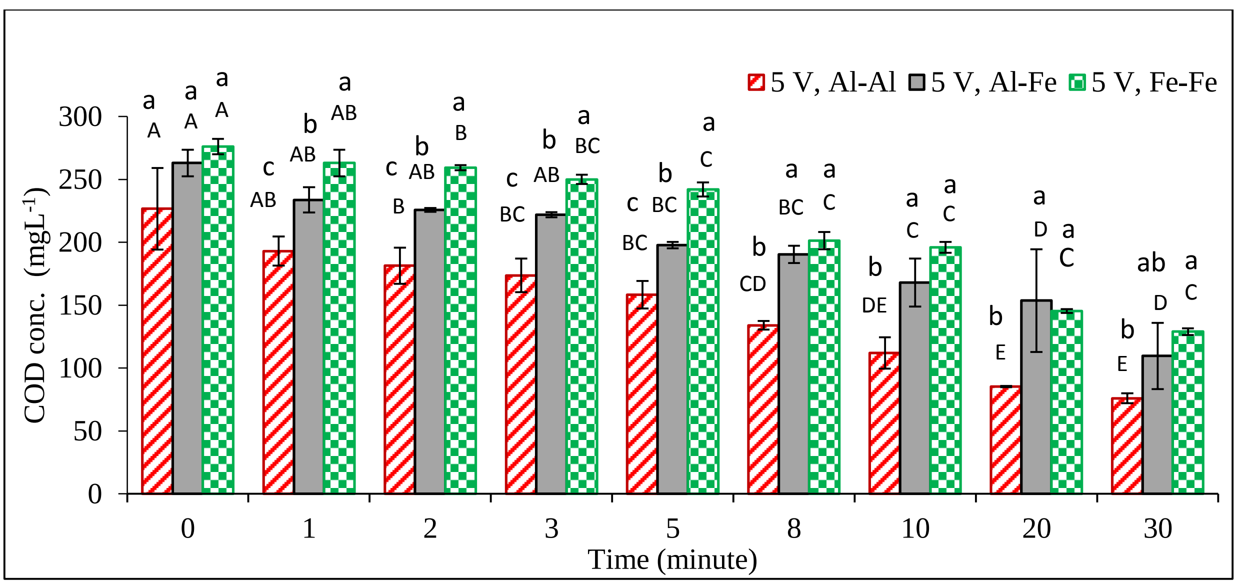

Figure 5.11. COD value due to 5 V applied potential by different electrodes. Bar with the same capital letter and the same electrode are not significantly different at each sampling time over the experiment period. Similarly, the same small letter for the same sampling time and different electrode are not significantly different fromeach other at p≤0.05.

5.7. Comparison of TP, TN, and COD reduction

For 30 minutes treatment times, the TP reduction was the highest for all electrode types followed by the COD and TN reduction for each levels of applied voltage potential (Figs. 13, 14 15). The TP reduction was about 100% in all three voltages potentials (5 V, 10 V and 15 V) within 30 minutes of treatment times. Though the percentage reduction of TN and COD increased with the increasing applied voltage potential levels, it did not reach to 100% under tested conditions (30 minutes). The higher TP reduction was likely due to formation of abundant amount of insoluble metal phosphate when OH^- released from the cathode react with the soluble phosphate ions already contained in the feedlot runoff during electrolysis process according to equations 8 to12 (Dinh-Duc et al., 2014; Inan & Alaydin, 2014). Though the reduction of COD was greater than TN, it was lower than TP. Average COD reduction was >60% and the main reason of COD reduction was the electrolytic oxidation and electrolysis process of organic and inorganic carbon present in the feedlot runoff. The higher percentage of COD reduction could be due to the presence of simple oxidizable carbon compound or suspended solids and liquids (Moreno-Casillas et al., 2007; Yun et al., 2014). TN reduction was the lowest (<60%) and lower TN reduction rate could be due to lower denitrification and ammonia stripping process (Emamjomeh & Sivakumar, 2009; Ilhan et al., 2008; Yun et al., 2014).

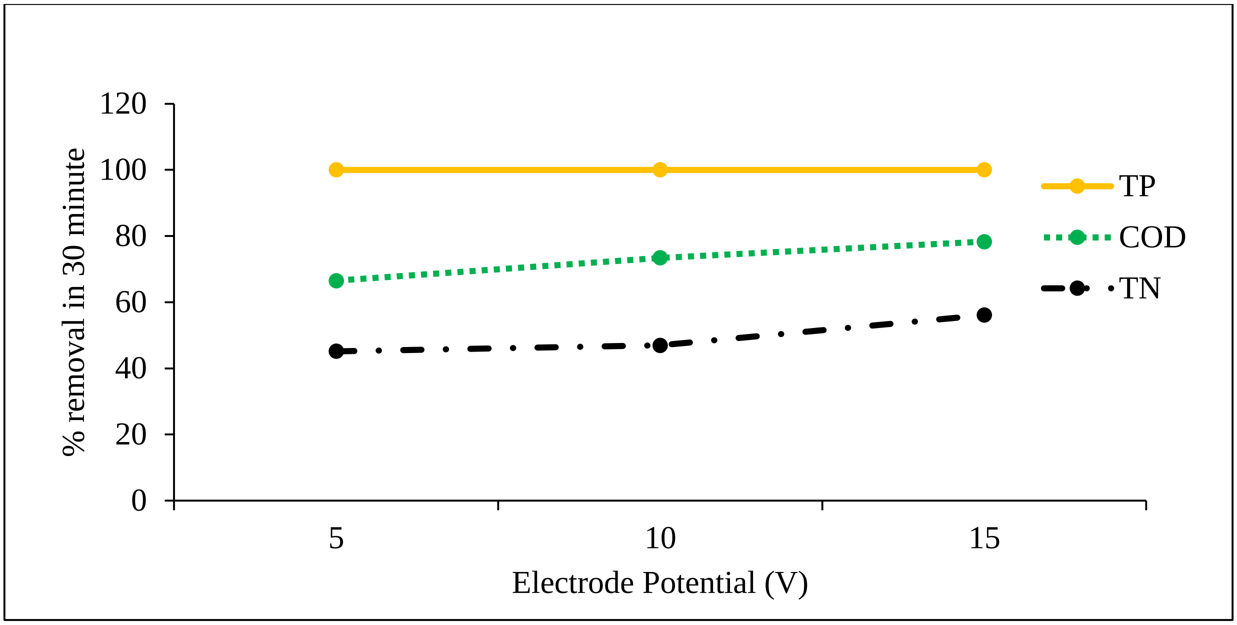

Figure 5.12. TP, TN and COD percentage reduction by Al-Al electrodes.

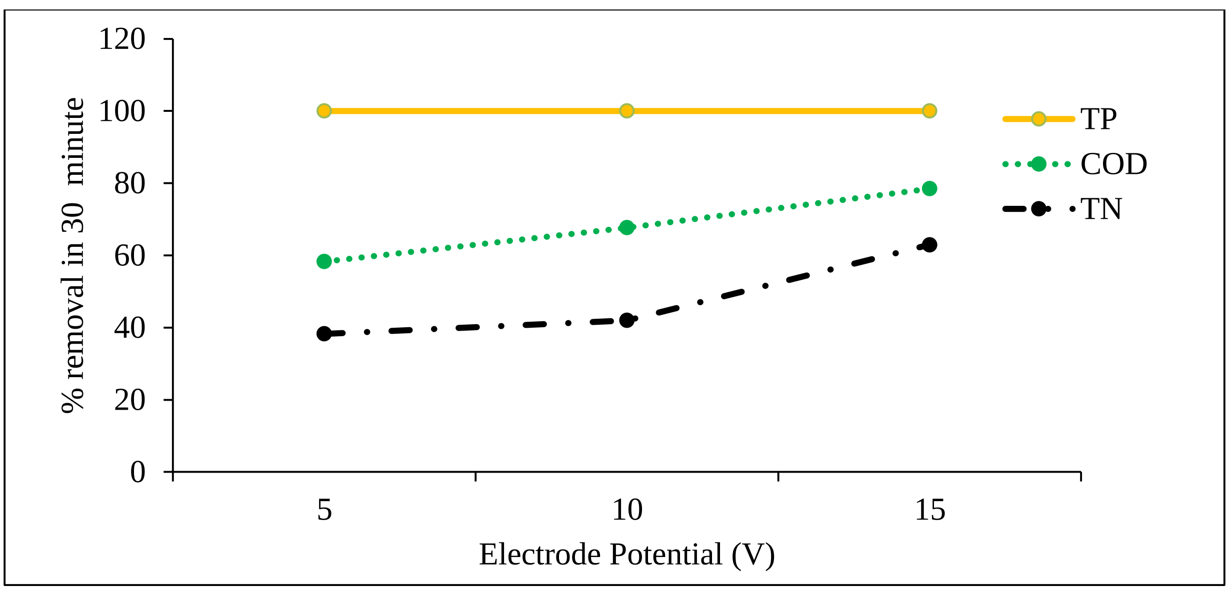

Figure 5.13. TP, TN and COD percentage reduction by Al-Fe electrodes.

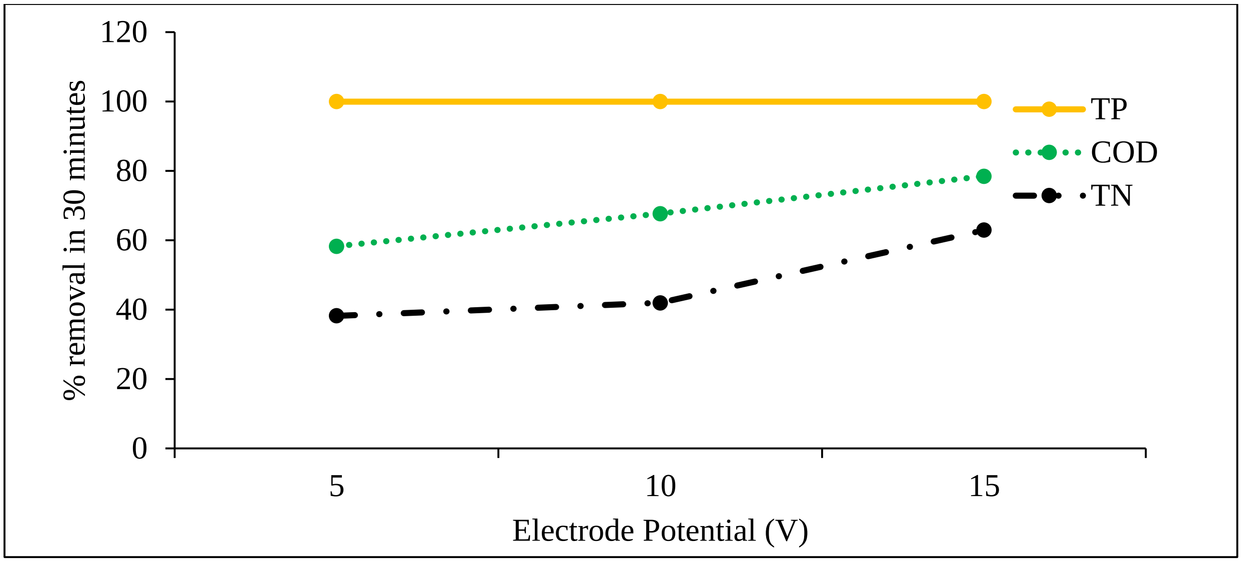

Figure 5.14. TP, TN and COD percentage reduction by Fe-Fe electrodes.

5.8. Specific Electrical Energy Consumption

For the same 30 minutes treatment time, the SEEC (Energy required per unit TP, TN or COD reduction, or per unit volume of feedlot runoff) was higher for 15 V applied potential than the 10 V and 5 V applied potential (Table 5.2). It was also observed that treatment time decreased with increased applied voltage potential for the same amount of TP, COD and TN reduction. Therefore, at higher applied electrical potential, the treatment time of electrolysis can be reduced which is preferable for designing continuous or higher capacity batch reactor for treating feedlot runoff under field condition. In general, from this research, TN showed the highest SEEC per kg removed followed by COD and TP (Table 5.2). Both Al-Al and Al-Fe electrodes performed equally, removed 100% TP at similar SEEC, and outperformed Fe-Fe electrodes. The lowest SEEC per kg TP removed was estimated 7.98 for Al-AL electrodes. Similarly, the lowest SEEC per kg COD and TN removed were estimated as 4.77 and 70.89 kWh/pollutants (Table 5.2). In this research, aluminum based electrodes (Al-Al and Al-Fe) removed more TP and COD compared to Fe-Fe electrodes. This was likely due to excess active ionization when aluminum ion combined with the OH^- and contributed to the generation of higher amounts of $Al(OH)_3$ (Hong et al., 2013; Lindsay et al., 1996; Rahman, S. & Borhan, 2014).

5.9. Characteristics of sludge by different electrode in electrolysis

The elemental analysis results of sludge shows that the hybrid (Al-Fe) electrode produced both Al and Fe element residue, but less in quantity than the Al-Al or Fe-Fe electrodes (data not shown). The aluminum reside produced by hybrid (Al-Fe) electrodes were 55.38%, 51.06%, and 37.56% less than the aluminum residue produced by aluminum electrode at 15 V, 10 V and 5 V electrode potential, respectively. Similarly, iron residue produced by hybrid (Al-Fe) electrode were 43.91%, 48.50%, and 63.18% less than the iron residue produced by iron electrodes at 15 V, 10 V and 5 V electrode potential, respectively. Aluminum electrodes produced more Ca, Cu, K, Li, Mg, Pb, S, Ti, and V residue than the hybrid (Al-Fe) and iron electrode. Similarly, iron electrode produced more Ag, As, Cd, Ce, Co, Mn, Ni and Tl residue than the hybrid and aluminum electrode. Except iron residue produced by the iron electrode and aluminum residue produced by aluminum electrode, and both residue presented for hybrid electrode, rest of all elemental residue of the metal presented in sludge were due to the sedimentation of metal residue in a sludge during an electrolysis. Therefore, it also proved that electrolysis help to remove metals presented in the feedlot runoff. The total amount of element residue produced by the electrolysis is present in Table 5.3.

Table 5.2. Comparison of removal efficiency and energy consumption for three applied electrical potential at 30 minutes electrolysis time.

Electrical Potential	Current density (A/cm^2)	Percent change		Removal efficiency (%)			Energy (Kwh/ m^3)	Specific Energy Consumption (KWh /kg pollutant removed)		
		EC	pH	TP	COD	TN		TP	COD	TN
Al-Al electrode										
15 V	0.036	13.28	-7.55*	100	78.28	56.07	26.02	62.26	61.19	651
10 V	0.020	9.72	-1.79*	100	73.39	46.93	9.85	29.24	24.92	321
5 V	0.010	5.82	5.57	100	66.47	45.16	2.50	7.98	8.30	89
Al-Fe electrode										
15 V	0.023	18.97	-2.98*	100	78.48	62.96	16.39	26.53	39.66	482
10 V	0.017	8.10	6.94	100	67.67	42.00	8.27	20.96	23.06	295
5 V	0.006	2.96	-0.88*	100	58.30	38.27	1.46	10.18	4.77	71
Fe-Fe electrode										
15 V	0.032	6.10	-22.2*	100	76.75	41.44	22.99	37.65	55.28	7412
10 V	0.022	5.56	-16.0*	100	67.12	37.61	10.37	33.39	43.61	379
5 V	0.010	3.57	-15.9*	100	53.26	27.35	2.30	20.25	23.47	119

*- sign indicate the increase in value than initial

Table 5.3. Elemental analysis value of metal residue produced from the electrolysis of the feedlot runoff.

S.N.	Elements	Al-Fe 15V	Al-Fe 10V	Al-Fe 5V	Fe-Fe 15V	Fe-Fe 10V	Fe-Fe 5V	Al-Al 15V	Al-Al 10V	Al-Al 5V
1	Ag	1.14b± 0.09	1.04b± 0.13	0.76bc± 0.12	2.30b± 0.12	2.25a± 0.04	2.18a± 0.14	2.34bc± 0	MLD	MLD
2	Al	87312d± 6199	83862d± 57251	84735d± 10976	821e± 379	91e± 92	34e± 14	195703a± 11461	171373b± 3829	135707c± 6657
3	As	64b± 2.5	65b± 6.1	52bc± 3.3	120a± 2.7	127a± 2.7	127a± 2.3	130bc±0	10c± 4.2	16c± 0.7
4	B	10.5d± 2.8	10.5d± 0.5	21.4bc± 5.9	18c± 1	25.9b± 3.1	39.7a± 0.3	23.3b± 1.4	21.6bc± 1.4	23b± 1.8
5	Ba	14.65b± 1.76	12.06bc± 3.52	30.68a± 8.34	18.05b± 2.91	6.90c± 1.27	12.56bc± 0.52	7.13c± 2.02	12.98bc± 2.35	26.68a± 2.23
6	Ca	10596 ef± 1112	12195 de± 1067	23821a± 1725	13536 cd± 832	8970f± 1119	13005 cd± 925	14698c± 113	16574b± 636	17972b± 352
7	Cd	5.35b± 0.31	5.02bc± 0.66	3.74cd± 0.11	8.06a± 1.28	7.81a± 1.55	7.25a± 1.06	2.69de± 0.10	2.31de± 0.02	1.90e± 0.10

(continues)

Table 5.3. Elemental analysis value of metal residue produced from the electrolysis of the feedlot runoff (continued).

S.N.	Elements	Al-Fe 15V	Al-Fe 10V	Al-Fe 5V	Fe-Fe 15V	Fe-Fe 10V	Fe-Fe 5V	Al-Al 15V	Al-Al 10V	Al-Al 5V
8	Ce	12.09b± 0.37	10.21b± 1.16	8.01bcd± 1.86	23.47a± 0.85	22.13a± 0.50	20.12a± 0.82	21.01bcd± 0	1.73d± 0	3.24cd± 0.18
9	Co	7.41c± 0.03	7.40c± 0.51	7.79c± 0.61	12.89b± 0.43	13.43b± 0.19	15.08a± 0.68	2.14f± 0.1	2.96e± 0.13	4.21d± 0.15
10	Cu	47.02abc± 11.44	45.96abc± 8.85	67.93a± 11.07	33.98c± 8.22	40.96bc± 12.11	45.89abc± 24.61	62.49ab± 11.20	64.96ab± 8.44	60.33ab± 6.34
11	Fe	107299c± 6400	98460c± 12223	74618d± 6876	191328b± 545	191203b± 577	202696a± 24780	1214e± 237	1312e± 188	2194e± 336
12	K	4438c± 51	4783 bc± 482	6266a± 207	4195c± 633	3999c± 252	4742bc± 398	6532a± 367	4742bc± 182	5279b± 751
13	Li	28.41a± 8.14	32.02a± 1.58	17.18b± 9.24	2.85c± 0.40	1.50c± 0.22	1.96c± 0.23	28.59a± 1.07	33.83a± 1.16	34.57a± 1.36
14	Mg	20227b± 599	21843a± 194	21689a± 1430	11622d± 833	15239c± 527	11208d± 372	20197b± 656	22866a± 369	21942a± 1023

(continues)

Table 5.3. Elemental analysis value of metal residue produced from the electrolysis of the feedlot runoff (continued).

S.N.	Elements	Al-Fe 15V	Al-Fe 10V	Al-Fe 5V	Fe-Fe 15V	Fe-Fe 10V	Fe-Fe 5V	Al-Al 15V	Al-Al 10V	Al-Al 5V
15	Mn	326b± 13	272c± 18	306b± 16	516a± 11	494a± 13	503a± 26	149f± 9	174e± 4	224d± 5
16	Na	1236b± 54	1354b± 17	1265b± 69	1231b± 24	1260b± 75	1378b± 14	1869a± 11	1218b± 18	1261b± 24
17	Ni	44.1b± 1.08	39.3b± 3.74	31.6c± 1.52	71.9a± 5.23	73.4a± 2.07	71.9a± 7.75	13.3d± 1.35	15d± 0.87	17.0d± 0.51
18	P	4829e± 362	6418d± 362	15381a± 392	3583f± 310	4708e± 562	9493b± 407	3316f± 260	5235e± 141	8336c± 425
19	Pb	76d± 6.5	75d± 5.9	75d± 10.7	-22f± 0.3	-23f± 0.8	MLD	169a± 9.6	152b± 2.9	126c± 7.1
20	S	13707a± 1157	14068a± 586	7729c± 1195	5585d± 939	6661cd± 215	6889cd± 373	15048a± 632	13956a± 123	10500b± 672
21	Sb	MLD	MLD	MLD	MLD	MLD	MLD	MLD	MLD	MLD

(continues)

Table 5.3. Elemental analysis value of metal residue produced from the electrlysis of the feedlot runoff.

S.N.	Elements	Al-Fe 15V	Al-Fe 10V	Al-Fe 5V	Fe-Fe 15V	Fe-Fe 10V	Fe-Fe 5V	Al-Al 15V	Al-Al 10V	Al-Al 5V
22	Se	MLD	MLD	9.99	MLD	MLD	MLD	9.69	8.86	7.05
23	Si	73b± 11.3	59b± 10.2	186a± 119.7	72b± 24.4	64b± 12.0	89b± 16.6	84b± 10.4	86b± 17.4	43b± 1.8
24	Sn	3.3ab± 0.73	2.8ab± 0.50	3.7ab± 0.61	3.7ab± 0.22	3.5ab± 0.85	4.1a± 1.33	4.1a± 0.08	2.7b± 0.11	2.1ab± 0.12
25	Ti	9.7bcd± 2.01	5.3de± 2.12	11.7bc± 7.44	7.5cd± 1.59	1.7e± 1.67	1.5e± 0.40	11.2bc± 1.42	13.7ab± 1.63	18.0a± 0.75
26	Tl	6.3b± 2.33	6.7b± 0.75	MLD	10.6a± 0.83	10.1a± 0.63	9.2a± 0.57	4.6bc± 1.27	5.0c± 1.33	MLD
27	V	15.6b± 2.02	15.3b± 0.62	20.0a± 0.50	13.2c± 0.73	13.0c± 0.33	16.8b± 0.33	19.5a± 1.61	20.5a± 1.29	20.4a± 0.26
28	Zn	536.5a± 564.37	62.8a± 21.54	274.7a± 187.64	406.1a± 554.16	49a± 6.39	51.5a± 15.61	329.4a± 217.09	53.3a± 7.94	58.1a± 9.06

* Same small letter for different electrode and potential for same element are not significantly different at $p \leq 0.05$

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusion

In this study, hydroponic and electrolysis experiments were conducted to determine effectiveness of nutrient runoff remediation from the feedlot runoff. In hydroponic experiment, both feedlot runoff and Hoagland solutions were used to compare plants (sorghum, water lettuce and water hyacinth) net biomass production, and nutrient removal capacity under ideal and actual nutrients condition. The electrolysis process, feedlot runoff was treated with three different types of electrodes (Al-Al, Fe-Fe, and Al-Fe) at different electrode voltage level for a designated time. Both studies were effective in removing nutrients, but depending on target nutrient, a specific treatment can be designed. Conclusions based on these two methods are listed below:

6.1.1. Hydroponic experiment

- All plants grew well in both runoff and Hoagland solution and removed nutrient considerably. Sorghum outperformed other plants in terms of biomass growth and nutrient removal.
- Diluting feedlot runoff had little effect in nutrient reduction.
- No significant changes in pH in runoff were observed during the plant growth.
- All plants significantly reduced EC from the feedlot runoff samples. Irrespective of experiment period, sorghum reduced EC significantly more than those of water hyacinth and water lettuce from feedlot runoff in second batch.
- Sorghum reduced significant amount of NO_2-N+NO_3-N from Hoagland solution in both batches, but in feedlot runoff, sorghum and water lettuce reduced significant amount of NO_2-N+NO_3-N in first batch.

- Similarly, water hyacinth reduced TKN concentration significantly better than the sorghum and water lettuce in both batches Hoagland solution but it was same for all plants in feedlot runoff in both batches.
- TP reduction was outperformed by sorghum than the water hyacinth and water lettuce in Hoagland as well as feedlot runoff in both batches.
- Amount of nutrients in runoff is very important to grow plants, but it was not a limiting factor in this study

6.1.2 Electrolysis process

- Electrolysis treatment was very effective in reducing EC, TP, TN and COD from runoff within 30 minutes of treatment.
- TP percentage reduction was higher than the TN and COD.
- Al-Al electrode seems to be more effective than the other two electrodes for TP reduction. Similarly, Al-Fe electrode reduced TN better than other two electrodes and Al-Al electrode reduced COD better than other two electrodes at low applied electrode potential although there were no significant differences among three electrode at higher applied electrode potential.
- This experiment also indicate that higher electrode potential was faster for TP, TN and COD but consumed higher amount of electric energy for the same amount of TP, TN and COD reduction as compared to lower electrode potential.

6.2. Recommendations

- This study was conducted in batches. A continuous system may be developed to test the effectiveness of both systems.

- Electrolysis may be implemented for a short period of time before spreading runoff to downstream, where sorghum may be seeded to treat runoff further.
- Further study can be conducted to find out more salt tolerant plants to reduce nutrients from runoff and to reduce environmental concern.
- Electrolysis and hydroponics treatment process will be very effective if it will be coupled with other advanced wastewater treatment process such as reverse osmosis or membrane technology because in both process, the nutrient and sediment load have already reduced at lower level which is suitable for the further advance wastewater treatment process.

6.3. Limitations/Future works

- Hydroponic technique may be used for nutrient reduction in feedlot runoff treatment. Among three plant varieties, sorghum produced higher biomass and reduced nutrients better than water hyacinth and water lettuce. Therefore, sorghum may be used to treat feedlot runoff to reduce feedlot nutrient contribution downstream. Electrolysis may be used for quick nutrient reduction, especially phosphorus reduction, than the hydroponic technique because in hydroponic technique requires longer time and space than the electrolysis process for same amount of nutrient reduction.
- The effluent from the electrolysis process should be analysis and treated because it has metal hydroxide contamination that can increase soil and water alkalinity after contamination and as medium which may not help for plant growth.
- Electricity energy costs required in the electrolysis process increased the running cost of feedlot runoff treatment process. Therefore, before choose one of these option, availability and cost of electricity as well as availability of space and suitability of environment should be considered.

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